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Pelletized drinking water treatment residuals for the removal of arsenic and phosphate from water

KWR Watercycle Research Institute

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Managementsamenvatting

Pellets van waterijzer: effectieve adsorbentia voor fosfaat en arseen.

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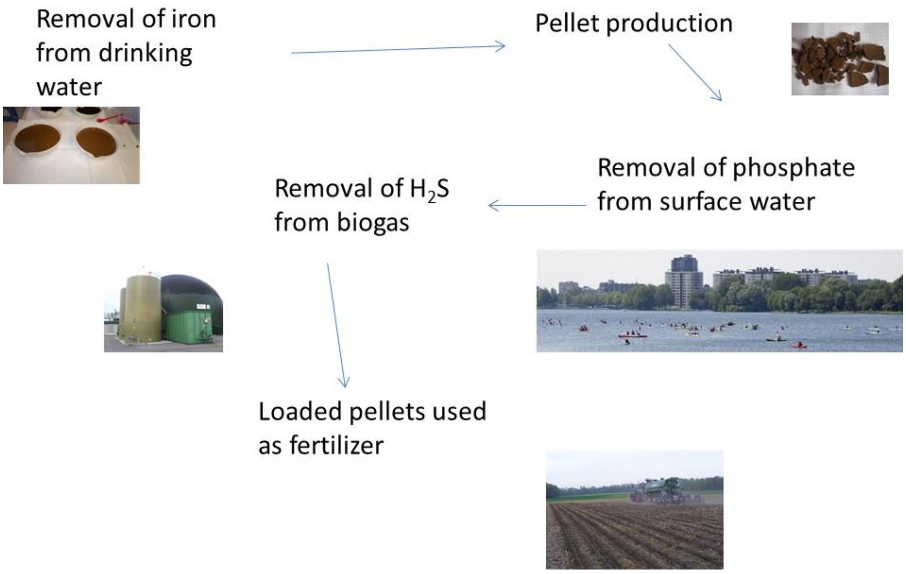
Uit eerder onderzoek was gebleken dat waterijzer, een bijproduct van drinkwaterproductie, een goed adsorbent kan zijn voor fosfaat. Bovendien was uit de literatuur bekend dat ijzer(hydr)oxiden ook arsenaat kunnen adsorberen. In dit onderzoek is door middel van laboratorium- en pilot-experimenten bekeken in hoeverre (gepelletiseerd) waterijzer kan worden toegepast om fosfaat te verwijderen uit oppervlaktewater en arseen uit drinkwater. Om het materiaal beter te kunnen hanteren en transporteren zijn er pellets van gemaakt. Bovendien maken pellets het filtratieproces ook beter beheersbaar. Voor deze pelletisatie zijn verschillende methoden uitgetest. Bovendien zijn zowel waterijzer van verschillende drinkwaterproductielocaties als de pellets op diverse manieren gekarakteriseerd.

Waarschijnlijk is het mogelijk de pellets op een circulaire manier in te zetten, door ze eerst toe te passen bij de verwijdering van fosfaat uit oppervlaktewater, ze vervolgens te gebruiken om waterstofsulfide te verwijderen uit biogas, en ze daarna als kunstmest toe te passen.



Circulaire toepassing van waterijzer

Belang: Nuttige toepassing van reststof waterijzer, verwijdering van fosfaat uit oppervlaktewater, en verwijdering van arseen uit drinkwater

Een veel voorkomend probleem in oppervlaktewater zijn te hoge concentraties fosfaat. Hoewel de WHO een arseennorm hanteert van 10 µg/L hebben de Nederlandse Drinkwaterbedrijven zichzelf opgelegd die te verlagen tot 1 µg/L, wat betekent dat sommige bedrijven het gehalte arseen in hun drinkwater moeten verlagen. In beide gevallen zou waterijzer gebruikt kunnen worden om het probleem op te lossen, aangezien bekend is dat ijzer(hydr)oxide fosfaat en arseen kan adsorberen. Waterijzer is een reststof die vrijkomt bij de productie van drinkwater. Door er pellets van te maken is het eenvoudiger het materiaal te transporteren en toe te passen. Deze pellets kunnen worden gebruikt als filtermateriaal voor de verwijdering van fosfaat uit oppervlaktewater en van arseen uit drinkwater.

Aanpak: Karakterisering van materiaal, pelletisering, en adsorptie-experimenten op laboratorium- en pilotschaal.

Waterijzer, afkomstig van verschillende drinkwaterproductielocaties, werd op diverse manieren gekarakteriseerd. Daarnaast werden er drie methoden toegepast om het materiaal te pelletiseren: een kleinschalige labmethode, en twee methoden die ook op grotere schaal kunnen worden toegepast (extrusie onder hoge druk, en een “build up pelletization” methode zonder druk). Ook de gevormde pellets werden met diverse fysische en chemische methoden gekarakteriseerd.

De pellets werden op laboratoriumschaal getest in adsorptie-experimenten met fosfaat en arseen. Op deze manier werd geprobeerd vast te stellen welke eigenschappen de meeste invloed hebben op het adsorptiegedrag van de pellets.

Vervolgens werden de, via extrusie verkregen pellets, toegepast in drie verschillende pilot-opstellingen. Bij Waternet werden ze als filtermateriaal gebruikt voor de verwijdering van fosfaat uit oppervlaktewater van de Sloterbinnenpolder. Bij Dunea en Brabant Water werden de pellets als filtermateriaal gebruikt voor de verwijdering van arseen uit drinkwater.

Resultaten: goede adorbentia voor fosfaat en arseen.

Uit de experimenten bleek dat de samenstelling van waterijzer van verschillende locaties grote verschillen kan vertonen. Door gebruik te maken van een mengsel hiervan is het mogelijk om zowel een constante beschikbaarheid als een constante samenstelling van het materiaal te waarborgen. Het bleek dat vooral het ijzergehalte en het specifiek oppervlak van het materiaal van belang zijn voor de adsorptiecapaciteit.

De op het lab toegepaste methode om pellets te maken is niet geschikt voor grootschalige toepassingen. De methode met “build-up pelletization” heeft enkele voordelen in vergelijking met de extrusie-methode, maar meer onderzoek is nodig naar optimalisatie van dit proces. Hierbij is het van belang goede standaarden te formuleren, waaraan de pellets moeten voldoen, vooral ook wat betreft hun (mechanische) stabiliteit. De keuze en toepassing van een bindmiddel spelen hierin ook een belangrijke rol.

Experimenten lieten zien dat de pellets een goede adsorptiecapaciteit hebben voor fosfaat. In het pilot-experiment bij Waternet bleek het mogelijk gedurende minstens zes maanden het fosfaatgehalte van het oppervlaktewater te verlagen van ca. 0,7 tot 0,03-0,1 mg/L, wat een sterke kwaliteitsverbetering betekende. Door een “up-flow” proces te hanteren traden er geen problemen op met vervuiling van het filterbed.

De pilot-experimenten bij Dunea en Brabant Water toonden aan dat de pellets ook geschikt zijn om het arseengehalte van drinkwater tot onder de streefwaarde van 1 µg/L te verlagen. Tijdens deze experimenten, die ook gedurende een half jaar plaatsvonden, trad bij de met GIH gevulde kolommen, in tegenstelling tot die gevuld met Ferrosorp Plus, geen doorbraak op van arseen, waardoor het niet mogelijk was de maximale adsorptiecapaciteit vast te stellen.

Een punt dat wel verdere aandacht behoeft is lekkage van organische materiaal en mangaan uit de pellets aan het begin van het experiment. Mogelijk dat dit verminderd kan worden door een bepaalde samenstelling van het waterijzer te nemen, of door de pellets vooraf te wassen.

Implementatie: Verbetering kwaliteit oppervlaktewater en drinkwater; circulaire toepassing van waterijzer.

Door van waterijzer pellets te maken voor fosfaat- en arseenadsorptie is het mogelijk een reststof in te zetten om de waterkwaliteit te verbeteren. Uit onderzoek is inmiddels gebleken dat de met fosfaat beladen pellets kunnen worden gebruikt om waterstofsulfide te verwijderen uit biogas. Daarna kunnen de korrels mogelijk nog worden toegepast als kunstmest in de landbouw, waardoor de cirkel weer gesloten kan worden.

Rapport

Dit onderzoek is beschreven in rapport *Pelletized drinking water treatment residuals for the removal of arsenic and phosphate from water* **(KWR-2017.036).**

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Meer informatie
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Summary

From a previous TKI project it had been found that iron sludge, that is produced in drinking water facilities, can be used to adsorb phosphate. From literature it is known that iron(hydr)oxides also may be used to adsorb arsenate. In this project both applications were investigated, both on laboratory and on pilot scale. For easy handling the material had to be pelletized. Pelletization methods were improved, and the most important characteristics of the material and the pellets were determined.

Sludge characterization

It was found that sludge from various production sites may strongly vary in composition, e.g. in iron content and specific surface area. Besides, in “old” sludge crystallization may have taken place, as a result of which the surface area and adsorption capacity (at least for phosphate) will have decreased. In order to understand adsorption behavior of sludges from different drinking water facilities the material was characterized using various physical and chemical methods. It was found that large differences may occur between sludges. In order to ensure constant availability and quality of the adsorbents it is advised to use a mixture of iron sludges from different locations.

Pelletization

In order to improve handling of the sludge, the material will have to be pelletized. At the laboratory this was done by dissolving a binder (carboxymethyl cellulose; CMC) into the wet sludge (ca. 10% solids). The material then was dried, crushed and sieved to obtain the desired particle sizes. This method now was applied to some sludges from different drinking water facilities, and for the mixture of sludges.

As the laboratory pelletization method cannot be applied on a large scale, two different pelletization methods were applied to produce granular iron hydroxide (GIH) from Spannenburg sludge:

1. Drying with waste heat, using an electric mole, followed by extrusion under high pressure
2. Drum drying, followed by pelletization by means of a build-up pelletization process

The pelletization process still has to be further optimized for transport and handling of the pellets, taking into account the ease of operation, dust formation, up-scaling possibilities and pellet characteristics (like mechanical stability and adsorption capacity), but so far best results seemed to be obtained by applying the second method (build-up pelletization).

As a binder CMC was used, but if the sludge has a “high” dry solids content it is difficult to mix CMC with the iron(hydr)oxide. Cement and water glass also have been used as binders in the second “large scale” pelletization process. Although preliminary results seem to be good, for these materials more research still will be required.

Also the pellets obtained were characterized by means of different chemical and physical techniques, in order to determine which characteristics are most important for the

pelletization process and the application of pellets as adsorbents for phosphate and arsenate.

The pelletization processes and characterization of both sludges and pellets are visualized in Figure 1.

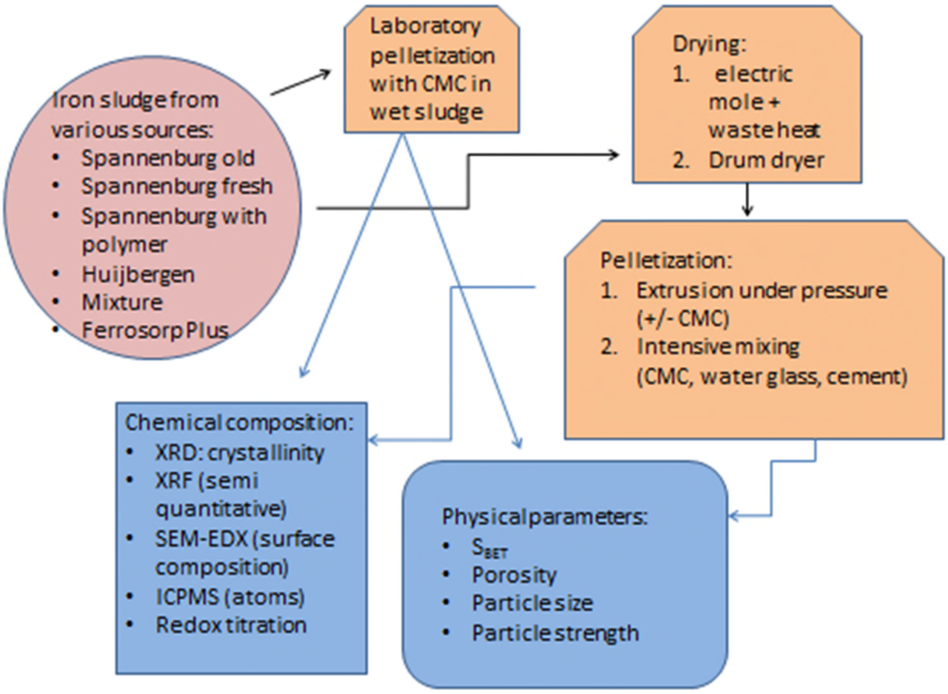

FIGURE 1:CHARACTERIZATION OF VARIOUS SLUDGES AND PELLETS.

Laboratory adsorption experiments

Using both pellets prepared at the laboratory and on a larger scale, phosphate and arsenate laboratory adsorption experiments were carried out. All pellets showed very good adsorption capacity for both phosphate and arsenate. Their performance was at least as good as the performance of a commercial adsorbent (Ferrosorp Plus).

Laboratory experiments showed that phosphate and As(V) adsorption were highest for Huijbergen sludge pellets, and lowest for Spannenburg “old” material. Spannenburg “fresh” and Ferrosorp Plus showed almost similar adsorption capacity. Also the pellets made from a mixture of sludges showed good adsorption capacity for both phosphate and arsenate. It was concluded that the adsorption capacity probably is related to the iron content of the material (a higher iron content resulting in a higher adsorption capacity), although also the specific surface area may play a role. Furthermore, there are some indications that the presence of polyacrylamide (sometimes used to dewater the sludge at the drinking water facility) decreases the adsorption capacity.

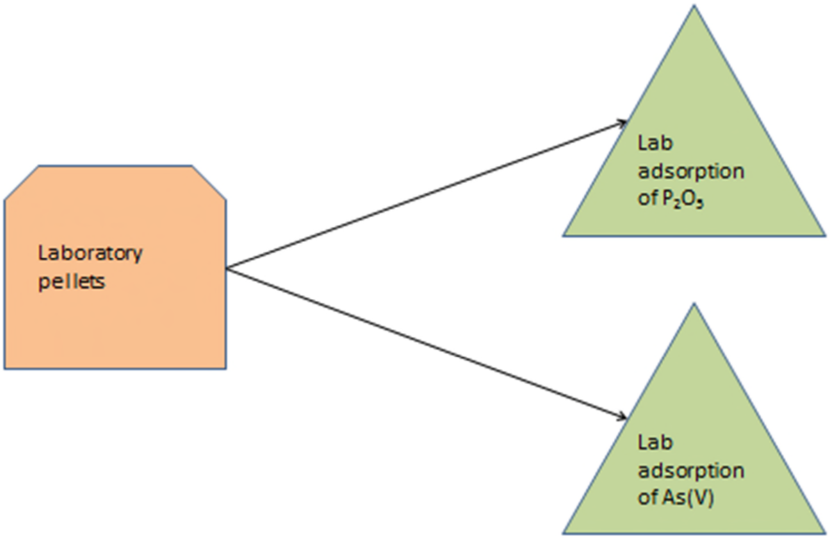

FIGURE 2: SCHEME OF LABORATORY ADSORPTION EXPERIMENTS

In the laboratory the cement and water glass GIH-pellets showed good As removal, and besides they seemed to be more stable than the previous pellets, prepared with CMC or without binder.

For different pellets the adsorption isotherms of phosphate and arsenate could be described by both the Langmuir and Freundlich model.

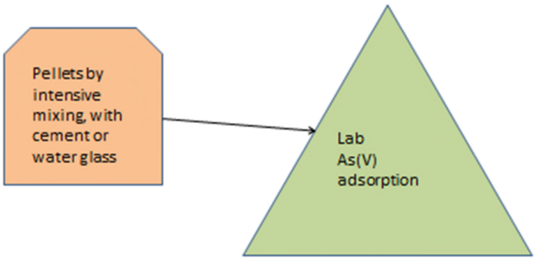

FIGURE 3: LABORATORY ADSORPTION EXPERIMENTS WITH CEMENT OR WATERGLASS CONTAINING PELLETS: GOOD As ADSORTPION

Pilot experiments on phosphate removal

It was decided to apply GIH, produced according to the first “large scale” process, in pilot experiments.

The first pilot experiments were aimed at phosphate adsorption in surface water from the Sloterbinnenpolder at Waternet. Three tanks containing a filter bed were used, and surface water was flown through it. One filter contained GIH with CMC, one contained GIH without CMC, and the third filter only contained sand. The effect of this filtration on phosphate removal was studied during six months. As up-flow was applied, pollution of the filter bed didn’t cause any problems. Furthermore, effective phosphate removal from the water to concentrations between 0.03 and 0.1 mg P/L was obtained during this period in both filter beds containing GIH, but not in the filter only containing sand. It was estimated that about 20 g P/kg Fe could be adsorbed at a residence time of about 20 min. It was concluded that phosphate adsorption by GIH significantly improved water quality over a period of at least six months.

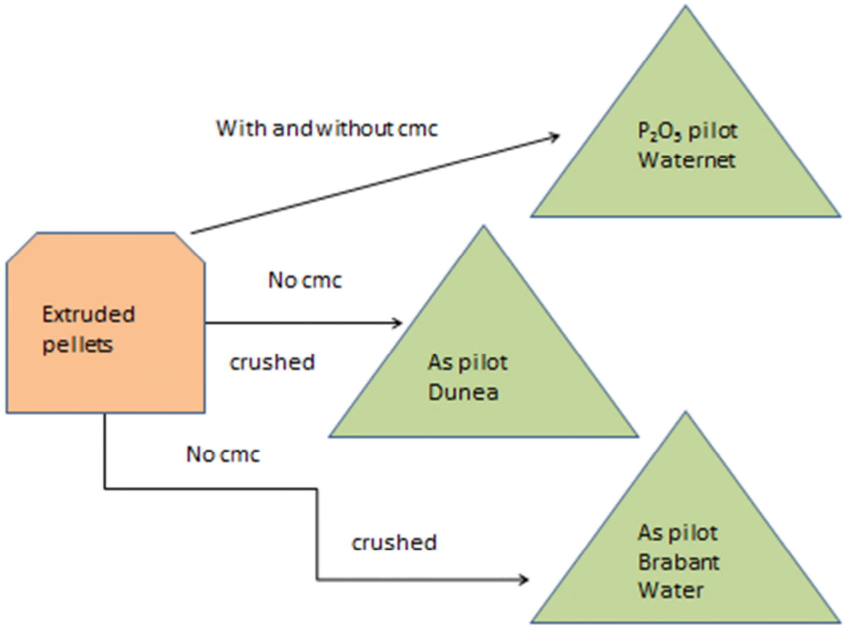

FIGURE 4: PILOT EXPERIMENTS WITH EXTRUDED PELLETS

Pilot experiments on arsenate removal

Arsenate removal was tested in column experiments at Dunea and Brabant Water. For these pilot experiments the same type of GIH (without CMC) was used as for the Waternet pilot. However, in this case the extruded pellets had been crushed before addition to the columns. In this way pellets were obtained of about the same size as the Ferrosorp pellets, that were used as a reference material.

In Katwijk (Dunea) five columns were applied: three containing GIH (with different empty bed contact times; EBCTs) and two containing Ferrosorp Plus (with different EBCTs) as a reference. In Prinsenbosch (Brabant Water) two columns filled with GIH were applied. Both pilots were operated during a period of about six months.

In both pilots it was found that high As-removal, to the target concentration of < 1µg/L, could be obtained, and no breakthrough was observed during the testing period. Increasing the EBCT resulted in a higher As removal. The As adsorption capacity appeared to be higher than had been expected, as a result of which the maximum adsorption wasn't reached during the pilot experiments, and maximum adsorption capacity for arsenate couldn't be determined. However, it can be concluded that GIH-pellets are suitable for As-removal. For design purposes an adsorption capacity of at least 240 mg As/ kg dry matter can be assumed at a residence time of 5 minutes.

Although the GIH filters appeared to be successful for arsenate removal, it was observed that leaching of some organic carbon and manganese may occur during the first period of operation. This leaching, and how to prevent it, will have to be studied in more detail.

Conclusions

In general it was concluded that pellets, made of iron sludge from drinking water facilities, are suitable for arsenate and phosphate removal from water. For transport and handling the pelletization procedure (i.e. drying, pelletizing and the choice of binder) still has to be optimized. One of the pellet characteristics, that still has to be optimized, is the mechanical and abrasion stability of the pellets. Furthermore, it should be realized that sludge composition, and thus adsorbent quality, may differ for various production locations, and possibly in time. Therefore, it is advised to use a mixture of sludges, in order to obtain constant adsorption capacity. This also ensures the permanent availability of the material.

For commercial GIH clear standards will have to be determined, regarding their composition (iron content, (absence of) crystallinity, porosity, surface area, presence of other compounds like organic material and other metals, and (mechanical) stability. It should also be decided by which standard method these properties should be characterized.

Contents

1 Introduction

1.1 Background

Drinking water treatment facilities generate a variety of residuals. Their physical and chemical characteristics depend mainly upon the raw water quality, the chemicals used for purification and the operating conditions of the purification process (Ippolito, Barbarick et al. 2011). The focus of this study is iron based drinking water treatment residuals and their potential to be used for the adsorption of arsenic (As) and (ortho)phosphate from water.

Groundwaters contain ferrous iron [Fe(II)], which upon aeration in drinking water treatment facilities is turned into iron(hydr)oxides. Likewise, when Fe(II) and/or ferric [Fe(III)] salts are added as coagulant, iron(hydr)oxides are formed. These iron(hydr)oxides ($Fe_2O_3.xH_2O$ with varying degrees of hydration) are removed from water during filtration. When the filters are backwashed, the iron(hydr)oxides end-up in the sludge of the treatment facilities. The sludge (residual) also contains constituents other than iron(hydr)oxides, such as organic matter, calcite, activated carbon particles, phosphates, silica sand particles, trace metals etc. Depending on origin (groundwater or surface water) characteristics of the iron sludge may vary, and thus also their application possibilities may vary.

In literature many studies have shown excellent performance of iron based drinking water treatment residuals in adsorbing orthophosphate in water and soil environments ((Persson, Nilsson et al. 1996, Gallimore, Basta et al. 1999, Ippolito, Barbarick et al. 1999, Haustein, Daniel et al. 2000, Elliott, O'Connor et al. 2002, Elliott, O'Connor et al. 2002, Dayton, Basta et al. 2003, Makris, Harris et al. 2005, Ippolito, Barbarick et al. 2011). The As adsorption potential of these residuals is also reported (Nagar, Sarkar et al. 2010, Caporale, Punamiya et al. 2013, Ociński, Jacukowicz-Sobala et al. 2016), however less extensively compared to orthophosphate.

In the Netherlands approximately 80 000 ton of iron based drinking water treatment residuals are produced yearly. The dry solids (DS) content of these residuals varies between 10 and 30%. Wet residuals are relatively difficult to handle, as they contain a high concentration of water. Transport of wet residuals to a site where they can be applied for orthophosphate or As removal is expected to involve high costs. The use of the residuals in dried form seems more practical (Hofman-Caris, Siegers et al. 2015). When Hofman-Caris et al. dried and sieved the residuals of two Dutch drinking water facilities in their laboratory experiments, the obtained granules were instable with respect to their crushing strength. However, when carboxymethyl cellulose (CMC) and bentonite binders were added to the wet residuals before drying, the strength of the produced pellets improved (Hofman-Caris, Siegers et al. 2015). Hofman-Caris et al. investigated the performance of Granular iron hydroxide (GIH) pellets for orthophosphate adsorption at laboratory scale and reported high adsorption capacity. However, As sorption potential was not yet explored, although from literature (Ippolito et al., 2011) it is known that iron(hydr)oxide may be used to adsorb arsenate..

1.2 Scope and objectives

The scope of this project includes development of a new As and orthophosphate adsorption medium having high capacity and compatibility, based on the iron based drinking water treatment residuals. Within this scope several experimental investigations were carried out.

Furthermore, the adsorbents were compared with a commercial adsorbent, also consisting of iron(hydr)oxides (Ferrosorp®). These include:

- A brief patent search to avoid interference with existing patents.
- A review of the quality and quantity of iron sludge in the Netherlands and identification the most suitable drinking water treatment facilities as a source of residuals to be used in full-scale production of GIH-pellets.
- The production of GIH-pellets by different methods and evaluation of the advantages and disadvantages associated with each method.
- The physicochemical characterization of GIH-pellets and Ferrosorp Plus.
- A study of As and orthophosphate adsorption performance of GIH-pellets produced from residuals of multiple drinking water treatment facilities at laboratory scale, and their comparison with the adsorption performance of Ferrosorp Plus.
- A study of As and orthophosphate adsorption performance of GIH-pellets and Ferrosorp Plus at pilot scale at three different drinking water companies.

1.3 Reading guide

The topics studied in this project were:

- Characterization of various iron sludges and a mixture of sludges
- Pelletization of iron sludge. For this different methods were used:
  - Laboratory pelletization, using CMC as a binder
  - Extrusion pelletization, with and without CMC
  - Rotating disc pelletization with water, with or without CMC as a binder
  - Rotating disc pelletization using cement or water glass as a binder
- Characterization of the pellets produced
- Laboratory phosphate and arsenic adsorption experiments
  - With laboratory made pellets with CMC as a binder
  - With pellets made using a rotating disc and cement or water glass as a binder (only arsenic adsorption)
- Pilot experiments on phosphate adsorption, using extruded pellets
- Pilot experiments on arsenic adsorption, using (crushed) extruded pellets

This report is divided into eleven chapters. This chapter, Chapter 1, sets the study background and an overview of key objectives. Chapter 2 describes the outcomes of the prior art study in existing patents. Chapter 3 describes the iron sludges studied, and drying and pelletization methods used in the experimental part. Chapter 4 describes the characterization of the pellets obtained. Chapter 5 describes the laboratory experiments on phosphate adsorption, and chapter 6 shows the pilot experiments on phosphate adsorption at Waternet. The results of laboratory and pilot experiments (at Dunea and Brabant Water) on arsenic adsorption are described in chapter 7 and 8 respectively. The conclusions of this research can be found in chapter 9, whereas an outlook on possibilities for full scale applications is given in chapter 10.

2 Prior Art Study

A limited patent search for European and worldwide patents, provided two patents of Lanxess, which were considered important for this study. These were EP 182505 and EP 1344564.

Patent EP 1582505 (applied in 2005) was evaluated by a European patent attorney, mrs. J. Verbart (De Vries @ Metman). She concluded that the GIH pellets prepared within the framework of the present study do not fall within the scope of the claims of the Lanxess patent, because the claims do not cover the presence of CMC as a binder in the GIH pellets. Furthermore, the GIH pellets have not been obtained with the process described in the product-by-process claim, nor are the resulting GIH pellets identical to products that have been obtained with the process according to the claim (for the full text of the evaluation see Appendix I).

For patent application (EP 1344564) an adapted version was filed in 2013. This patent was evaluated by Habbel & Habbel. For this new application, with regard to claim 1, Mr. Habbel reached the same conclusion as Mrs. Verbart: there is no problem, as our process fundamentally differs from the process described in the patent. However, there appears to be a remarkable wording in the new claims 6 and 7 of the revised version of EP 1582505. Where claim 6 states that one out of three products should be added to the pellets, claim 7 states that only one of these three products has to be used. According to the patent attorney this may quite well may be an editorial error, but if this is true, it might lead to a patent violation, if this adapted version of the patent will be granted. However, the attorney's conclusion partly is based on some information on our part, which was not available to Mr. Habbel at the time. Taking this into account, we are confident that there won't be any violation of EP 1582505. The full text of the evaluation can be found in Appendix II. In answer to his questions, the following points will be relevant:

1. In our process we never added a suspension. Only an aqueous solution of carboxymethyl cellulose (CMC) as a binder is added, which cannot be considered an ion exchange material. Neither activated carbon nor any other solid material is added to the Fe sludge. However, our Fe sludge may contain some aluminum compounds, which are already present in our starting material.

2. It has long been known that Fe sludge may contain small amounts of e.g. aluminum compounds, and that this Fe sludge can be used to adsorb e.g. phosphate from water. Examples of publications prior to 2002 are
   - report of the Delft University of Technology by Mr. Noijen (March 16th 1984)
   - report 1994-12 Toepassing drinkwaterslib RWZI; ISBN 90.74476.12.0 (1994)
   - a report by S. Thole; Verwertung von eisenhaltigen Wasserwerkschlämmen zur Phosphatelimination -aus kommunalem Abwasser, Prüfungsarbeit, Fortschrittberichte VD1-Verlag Reihe 15; Umwelttechnik nr. 117 (Oct. 1993).

   This clearly shows that the application mentioned in the patent was generally known (long) before the patent application was filed. However, until now this knowledge has not been made commercially applicable.

3. In the patent application it is mentioned that the material should preferably contain α-FeO(OH), and the particle size and specific surface area mentioned (and required for the adsorbent) are related to this specific material. From the publications mentioned above and from our own experiments it has become clear that the phosphate adsorption capacity of this crystalline material is much less than that of amorphous iron oxides. Therefore, in our investigations we use Fe sludge which contains amorphous irons oxides and preferably no or only a very limited amount of α-FeO(OH). Although the specific surface area of our particles is in the same range (as is the case for a wide variety of metal oxides used in industry), as such the claims on the specific surface area of α-FeO(OH) cannot be applied to our material, which has a different composition.

In the light of above discussion it can be concluded that the patents of Lanxess (c.q. Bayer) do not interfere with the GIH pellets produced and tested in the present study

3 Production of GIH-pellets and evaluation of pros and cons of different methods

3.1 Introduction

In this chapter materials and methods related to the production of GIH-pellets for laboratory scale and pilot scale adsorption experiments are described. Moreover, a description of alternative drying and pelletizing techniques, that were tested to optimize the production of GIH-pellets, is provided in this chapter. The (observed or measured) advantages and disadvantages associated with each method are discussed.

As a reference material Ferrosorp Plus, commercially available pellets, containing mianly iron(hydr)oxides, for adsorption purposes, is used in this report.

3.2 Production of GIH-pellets for laboratory scale adsorption tests

Several types of GIH-pellets were prepared at laboratory scale, using drinking water treatment residuals from various facilities. The residuals were mixed with a 2 wt% (based on solids) aqueous CMC solution using a magnetic stirrer. Subsequently the samples were dried at 105 ˚C in the laboratory oven, grinded and sieved, until a size range of 0.4-2.0 mm was obtained. For the laboratory scale adsorption tests several types of iron based drinking water treatment residuals were used to prepare the GIH-pellets. These include:

- Old residual from Spannenburg
- Residual from Spannenburg, taken freshly from the plant but been in stock at KWR for about one year
- Residual from Huijbergen
- Mixture of residuals from eleven drinking water treatment facilities

Figure 5shows the wet and processed drinking water treatment residuals at laboratory scale.

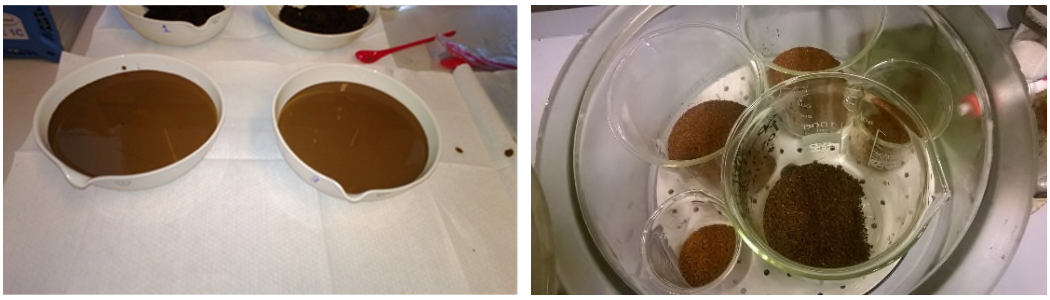

FIGURE 5 DRINKING WATER TREATMENT RESIDUALS BEFORE AND AFTER PROCESSING INTO PELLETS AT LABORATORY SCALE.

A distinction is made between the old and fresh residual from Spannenburg. The old residual refers to the residual in the stock pile of residuals at Spannenburg water facility. On the other hand, the fresh residual was obtained directly from the treatment process at

Spannenburg. The residuals from Huijbergen and that from the eleven facilities were all freshly produced.

Producing GIH-pellets from the mixture of eleven residuals was aimed at fullfilling the practical need of having consistent quality and adequate quantity of residuals as raw material for large scale GIH-production. To reach a favorable business case a mixture of residuals from eleven drinking water facilities was prepared, which was used for GIH-production at laboratory scale and subsequently evaluated by characterization and adsorption experiments in the laboratory. The following criteria were adopted for the selection of these eleven residuals.

- Source should be groundwater
- Frequently available (at least once per year)
- As content ≤ 75 ppm
- REACH registration of the source facility

This resulted in a mixture with the composition shown in Table 1 (based on the data of 2015). Mixing residuals in these proportions from the eleven facilities can produce 1540 ton DS of residuals.

TABLE 1: COMPOSITION OF MIXED SLUDGE FROM VARIOUS IRON SLUDGES.

Facility	**Production per year (Ton DS)**	**Share in the mixture (% DS)**
Ossendrecht	75.9	4.9
Hoogeveen	283.7	18.4
Huijbergen	31.3	2.0
Oldeholtpade	30.6	2.0
Roosendaal	37.8	2.5
Noordbergum	368	23.9
St. Jansklooster	207.5	13.5
Witharen	129.6	8.4
Bergen op Zoom	54	3.5
Nuland	51.8	3.4
Spannenburg	270	17.5
Mixture	1540	100

It should be noted that in this laboratory based method the pellets were produced under atmospheric pressure only. The binding was achieved by the addition of CMC to the matrix. It is not clear how the pellets produced by this process will behave in adsorption columns because in this study only batch adsorption experiments were carried out with the laboratory scale produced pellets. However, it should be marked that when magnetic stirring of >200 RPM was applied in some preliminary batch experiments, the pellets disintegrated. It can be argued that the disintegration was because of the interaction of pellets with the stirrers present in the glass bottles and not because of the agitation itself. Figure 6 shows the comparison between GIH-pellets and Ferrosorp Plus at the end of one of the experiments that was performed at mixing speed of >200 RPM. After this observation the mixing speed in batch adsorption experiments was fixed at 200 RPM.

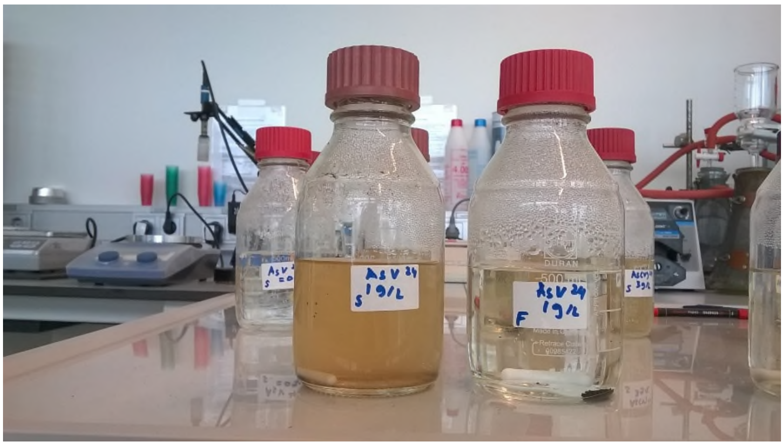

FIGURE 6 STABILITY OF GIH-PELLETS PRODUCED FROM FESH SPANNENBURG RESIDUAL (LEFT) VERSUS FERROSORP PLUS (RIGHT) WHEN MIXING SPEED OF >200 RPM WAS TESTED IN BATCH EXPERIMENTS.

Moreover, in batch experiments colored supernatant was noticed for some adsorbents. For example, Figure 6 shows the supernatant of GIH-pellets produced from the residual of Spannenburg. The dose of the pellets was increased from left to right (0.5 g/L to 5 g/L). In Figure 7 it can be seen that the intensity of color increased with the dosed mass of pellets. The color probably was due to the mobilization of organic compounds because all the supernatant samples that are shown here were pre-filtered through 0.45 µm filters to remove iron oxide particles.

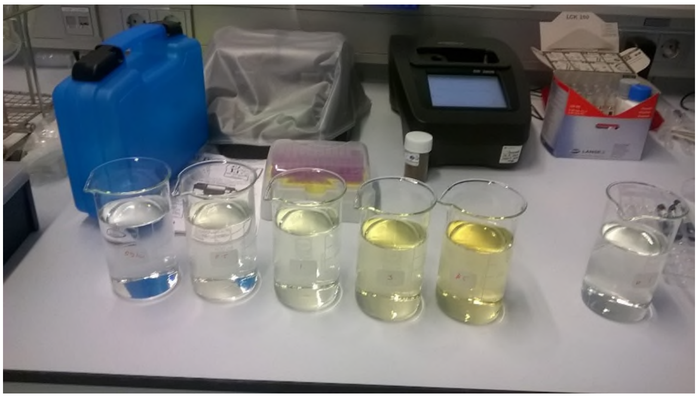

FIGURE 7 INCREASING COLORATION OF SUPERNATANT WITH INCREASE IN GIH-PELLETS DOSING FROM 0.5 (LEFT SIDE OF PICTURE) TO 5 g/L. (RIGHT SIDE OF PICTURE).

3.3 Production of GIH-pellets for pilot tests

For pilot tests, GIH-pellets were produced by Agravis Raiffeisen AG, based in Germany. Treatment residual from Spannenburg, a mixture of fresh and old residual (11.4% DS), was transported to Germany where the sludge was first dried and then pelletized by extrusion. The “old” material ≤ 5-6 years old. The production procedure differed from the laboratory based production method (see section 3.2) in that a different drying method was applied, pellets were produced by means of extrusion under relatively high pressure. Besides, in case CMC was added this was not dissolved in the solution, but added to the dried product.

Figure 8, Figure 9, and Figure 10 show some details of the production of pellets by Agravis. For the drying process waste heat of a biogas plant was used. The electric mole, shown in Figure 8, was used to move and mix the material during this process. The temperatures applied were relatively low, thus preventing crystallization of the iron(hydr)oxides. The main disadvantage of this process was the generation of lumps of semi-dried residual that had to be broken down for achieving the required dry solids (DS) content. Possibly, also the addition of a polymer to improve dewaterability of the sludge at the drinking water company before transport, also had some negative effects in the subsequent process. Moreover, the contamination e.g. twigs, stones etc. had to be removed manually or by sieving.

After drying, the material, with a DS content of 70-75%, was pelletized by extrusion pelletizing using the equipment shown in Figure 9. The pellet size obtained was 4-5 mm. A pressure of approximately 100 bar was applied to press the pellets. As later experiments revealed, this high pressure probably decreased the pore volume of the material, and thus the surface available for interaction with orthophosphate and As.

It should be noted that in this method the CMC solution was added after drying of the residual. It was not possible to add and mix CMC in the large quantity of pre-dried and lumpy sludge. Therefore, It is possible that the full binding capacity of CMC was not achieved in this way.

The GIH-pellets produced by the above mentioned extrusion method were used in the pilot experiment at Waternet for the removal of total and orthophosphate from surface water. These pellets were also used in the pilot tests for arsenate removal. However for these tests the pellets were crushed and sieved into a particle size range of 0.5-2.0 mm, in order to make it match the particle size of Ferrosorp Plus as a reference product.

FIGURE 8 DRYING OF SPANNENBURG RESIDUAL BY MEANS OF WASTE HEAT FROM BIOGAS PLANT AND ELECTRIC MOLE.

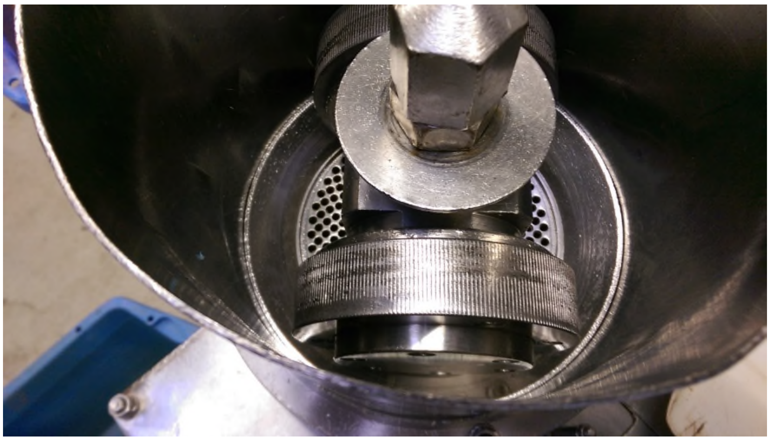

FIGURE 9 THE FLAT DIE PRESS USED FOR EXTRUSION PELLETISING.

Fertige GIH Ware NL

Bereich:
Futtermittelspezialprodukte

KWR – Pelletierung 2015

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FIGURE 10 GIH-PELLETS PRODUCED BY EXTRUSION.

The pellets made by Agravis under high pressure were analyzed for their phosphorous and arsenic contents by Labor Wessling GmbH. The results are presented in Table 9. The size of the pellets was about 2-10 mm, with a diameter of approximately 5 mm.

These pellets were applied in three pilot experiments: the pellets as such were used in the Waternet pilot for phosphate removal, and crushed pellets (with a smaller size) were used in arsenic adsorption experiments both in Katwijk (Dunea) and Prinsenbosch (Brabant Water). During these pilot experiments disintegration of GIH-pellets in the adsorption beds was observed and reported by the operators of the water facilities, indicating insufficient stability of the pellets.

3.4 Alternative drying and pelletization technique

As discussed in the previous section, the first batch of Spannenburg residual received by Agravis was dried by means of an “Electric mole” and waste heat. Because it wasn’t a continuous and automated process an alternative approach to dry and pelletize the residuals was sought.

Drinking water treatment residual was obtained from a German drinking water facility (Oldenburgisch-Ostfriesische Wasserverband; OOVW). This appeared to be a highly amorphous material, containing lower As and phosphate concentrations compared to the treatment residual of Spannenburg. The material was stored in a clamp for several weeks, during which the material was dried under the sun. As a result, the upper layer of the material was characterized by 40% DS, whereas the lower layer was characterized by approximately 20% DS. For further drying of this batch of residual a drum dryer was used. Advantages of this drying technique are that it is a continuous and automated process, which generates less dust. Furthermore, stones and twigs (organic material) could be removed automatically. Flue curing (using hot gasses originating from the burning of wood) was applied for heating. The maximum temperature in the drum was 80 °C, the DS content of the final material reached up to 85%.

FIGURE 11: DRYING BY MEANS OF AN ELECTRIC MOLE (LEFT) OR BY MEANS OF A DRUM DRYER (RIGHT).

After drying of residual in the drum dryer, “intensive mixing” was applied, in which a rotating mixing pan was used. The pellets were produced in a build-up pelletizing process. As for this process no pressure is required, the pore volume of the dried material probably was larger than the product obtained from extrusion pelletization process. It should be noted that contrarily to the continuous extrusion process, the intensive mixing process is a batch process. Pictures of the equipment used for both processes are shown in Figure 12.

FIGURE 12: PELLET PRODUCTION AT AGRAVIS. UPPER FIGURE: EXTRUSION PROCESS, APPLYING PRESSURE. LOWER PICTURE: INTENSIVE MIXING PROCESS.

The first trials with the intensive mixing process were carried out in the absence of any binder, as well as with CMC as binder. The pellets showed totally different behaviour under different circumstances. The pellets made without CMC appeared to be stable in water, but not during transport and storage. The pellets made with CMC showed the opposite behaviour: instable in water but stable during transport and storage (see Figure 13). A batch test for studying the adsorption capacity of As was started at KWR with these two types of GIH-pellets, however the test was terminated before completion because of the instability of the materials. This shows that CMC may not be regarded as the optimal binder for GIH-pellets, at least at the concentrations it has been used in the trials within this study.

FIGURE 13: STABILITY OF PELLETS IN WATER. LEFT PICTURE: WITHOUT CMC; RIGHT PICTURE: WITH CMC.

After it had become clear that CMC might not be the optimal binder, intensive mixing trials were carried out with two other types of binders: cement (1 and 5 wt % based on DS content) and sodium water glass (1and 5 wt % based on DS content). The cement based pellets were left in a closed plastic bag for four weeks to cure, the water glass based pellets were dried at 110 °C. Figure 14 shows the GIH-pellets containing cement and water glass as binders, pelletized by intensive mixing. It can be seen that the shape of these pellets is rounded, unlike the GIH-pellets produced by extrusion (Figure 10). Moreover, the pores seem more “open” when the pellets are of the product of intensive mixing.

The GIH-pellets produced by intensive mixing could not be extensively characterized in this study because of the limited time available for this project. It was noticed that the stability of the GIH-pellets that contained cement seemed to be better, at least these pellets did not disintegrate in the batch adsorption test in the presence of magnetic stirring of >200 RPM (the results of these adsorption tests are shown in paragraph 7.4). However, proper evaluation of the mechanical strength by an appropriate analysis technique, e.g. an abrasion test, should be performed before reaching a conclusion. Moreover, it must be noted that these batch experiments were of preliminary nature, and were conducted at an initial As concentration of 100 µg/L. It is likely that the influence of the nature and quantity of the binder on As adsorption capacity was not noticed at this low As concentration, however it may be more pronounced at higher As concentrations. Therefore, it is suggested to investigate the influence of different binding agents in a more extensive laboratory study.

3.5 Comparison of GIH-pellets production methods

Both production methods were evaluated, based on the production methods (costs of technical equipment and service, personal costs, the possibility to adjust the pellet size, and dust development), and the product quality (mechanical stability, porosity, BET surface area, pore distribution, adsorption capacity and binding material). The results are shown in Table 2 and Table 3. It is evident that the intensive mixing technique is ranked higher compared to extrusion on both technical and economic aspects. However, this ranking is based on several assumptions, especially related to the product quality. Further characterization (pre volume, specific surface area, attrition resistance, adsorption capacity for As and orthophosphate, kinetics etc.) of the GIH-pellets produced by intensive mixing is required to make a quantitative comparison.

TABLE 2: COMPARISON OF PRODUCTION METHODS ACCORDING TO AGRAVIS.

	Flat die press (extrusion)	**Build-up pelletization (intensive mixing)**
Costs production	-	+
Costs technical equipment	-	+
Costs employees	+	-/+
Costs service	-	+
Adjustment granular size	-	+
Dust development	-	-/+
Total	-	+

TABLE 3: COMPARISON OF PRODUCT QUALITY ACCORDING TO AGRAVIS.

	Flat die press (extrusion)	**Build up pelletizing (intensive mixing)**
Pellet stability	-	-/+
Additional drying	-/+	-/+
Pellet porosity	-	+
Pore distribution	-/+	+
BET surface area	-/+	+
Adsorption capacity	-/+	+
Crystallization risk	-	+
Total	-/+	+

+ good; -/+ medium; - bad

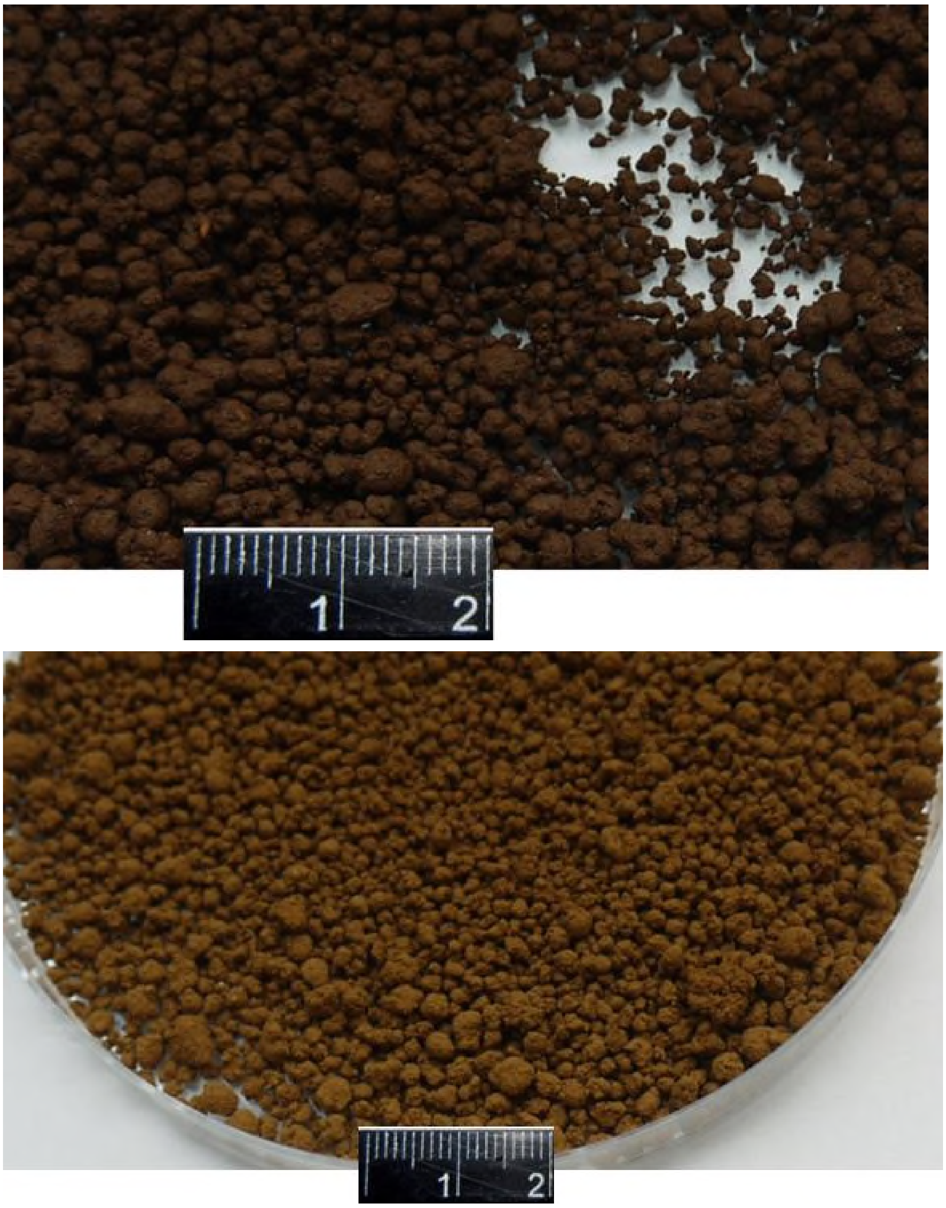


FIGURE 14: PELLETS MADE WITH DIFFERENT BINDERS, USING A DRUM DRYER AND INTENSIVE MIXING. UPPER PICTURE: CEMENT AS BINDING MATERIAL; LOWER PICTURE: SODIUM WATER GLASS AS BINDING MATERIAL.

3.6 Conclusions and recommendations

From the content presented in this chapter it can be concluded that the Dutch drinking water sector is capable of supplying approximately 1500 tons DS of appropriate quality drinking water treatment residuals for the production of GIH-pellets.

Because of the variation in sludge composition and in sludge availability, it was suggested to prepare GIH-pellets from a mixture of sludge from several (in this case eleven) ground water production plants. In this way it may be possible to ensure both permanent availability and constant quality of the adsorbents.

The pelletization procedure used at the laboratory is not suitable for up scaling. Therefore, other processes have been studied. The first process involved drying by means of waste heat and an electric mole, followed by extrusion under pressure. This process appeared not to be ideal: the drying caused a lot of dust, and because of the pressure the porosity of the materials became much smaller, which may affect their adsorption capacity.

The second process consisted of a drum dryer followed by intensive mixing. In this case no dust problems arose. The pellets made using cmc seemed to lack stability, and therefore later cement and water glass have been used as binding materials. This still has to be optimized.

The pelletization process for transforming the drinking water treatment residuals into an effective adsorbent needs further optimisation. This refers to the optimisation of the type and concentration of binder and the optimisation of the pelletization process itself. Stability of the product is critical. CMC, with a maximum tested concentration of 2% DS, does not appear to provide the required stability to the pelletized residuals. The intensive mixing process seems better compared to extrusion, however more empirical data (characterization, adsorption performance etc.) are needed to draw a final conclusion.

The product should be sufficiently stable to sustain all sorts of stresses (agitation, attrition etc.) during transport, handling and most importantly during actual use at the water treatment facilities. A laboratory scale procedure, representative of all these situations, is needed to determine the strength of the GIH-pellets in an appropriate manner. It is not very clear whether crushing strength is the parameter that should be optimized. Possibly, abrasion tests should give more information on the practical application of the pellets. Thus, it is recommended to optimize both the pellet production method, as well as the characterization of the pellet stability.

Furthermore, it has become clear, that different fields of application may require different properties of pellets (granular size, stability, specific surface area, crystallinity).

4 Chemical and physical characterization

4.1 Introduction

Both KWR and Agravis had GIH-pellets, both produced at laboratory scale and by Agravis at larger scale, and Ferrosorp Plus characterized by various chemical and physical methods, by different laboratories, in order to gather as much information about the media as possible. This chapter provides details about various characterization techniques that were used in this study and the outcomes of the analyses.

4.2 Materials and methods

Several techniques were used to characterize the GIH-pellets and Ferrosorp Plus. These include:

- Nitrogen (N_2) adsorption (for the determination of specific surface area (S_{BET}), pore size distribution and pore volume)
- X-Ray diffraction (XRD)(for identifying different mineral phases)
- X-Ray fluorescence (XRF) (for determining the elemental composition)
- Energy-dispersive X-ray spectroscopy (SEM-EDX) (for studying the surface morphology and composition)
- Crushing strength (for determining the compressive strength)
- Titration based techniques to determine the ratio of amorphous to crystalline iron

N_2 adsorption, X-Ray diffraction and X-Ray fluorescence analysis were conducted at Delft Solid Solutions (DSS) laboratory in the Netherlands. SEM-EDX analysis was carried out at Advanced Technology Research and Application Center of Selcuk University in Turkey. The X-Ray spectroscopy and crushing strength investigations were carried out by Agravis in Germany.

4.2.1 N_2 adsorption

Prior to the N_2 adsorption measurements, samples were degassed in vacuum at 90°C for 16 h. The dry sample weight obtained after the pre-treatment was used in the various calculations. Adsorption and desorption isotherms with N_2 as adsorptive solute were then recorded at 77 K on a Micromeritics TriStar 3000.

In N_2 physical gas adsorption, the sample cell holding the degasified sample is evacuated and cooled to liquid nitrogen temperature (77 K). Portions of nitrogen are dosed into the sample cell and will be partly adsorbed on the surface, eventually getting into equilibrium with the gas phase. In this way adsorption and desorption points are recorded at different pressures and the ad- and desorption isotherm can be constructed.

Adsorbed N_2 will first form a quasi-monolayer on the sample surface while further increase in pressure results in the formation of multilayers. In the region where monolayer and multilayers are formed, the specific surface area (S_{BET}) is determined according to the BET (Brunauer, Emmet and Teller) theory. This model is applicable to non-porous and meso- and macro-porous materials, and adsorption points in the relative pressure range between 0.05 and 0.25 are typically used. In case meso pores are present in the sample under investigation, N_2 will condense in these pores at higher relative pressures. This information can be used to derive a meso pore size distribution, typically by means of the so called BJH (Barrett Joyner and Halenda) pore size model. Besides, the empirical t-plot methodology can be used to discriminate between contributions from micro pores and remaining porosity (i.e. meso porosity, macro porosity and external surface area contributions). It must be noted that the size range of micro-pores is d_p<20Å, of meso-pores is 20Å ≤d_p≤500Å and of macro-pores is >500Å. d_p stands for pore diameter.

4.2.2 X-Ray Diffraction

The atomic and molecular structure can be attained by X-ray diffraction investigations. Crystalline atoms cause diffraction of an X-ray beam into specific directions, leading to typical reflections at certain characteristic positions in the XRD profile. In that way, the presence of crystalline matter can be identified; amorphous matter typically results in very broad, ill-defined reflections.

The X-ray powder diffraction (XRPD) patterns were recorded in a Bragg-Brentano geometry in a Bruker D5005 diffractometer equipped with Huber incident-beam monochromator and Braun PSD detector. Data collection was carried out at room temperature using monochromatic Cu radiation ($K\alpha1$ λ = 0.154056 nm) in the 2θ region between 15° and 95°, step size 0.035 degrees 2θ.

The sample, of about 30 milligrams, was deposited on a Si <510> wafer and was rotated during measurement. Data evaluation was done with the Bruker program EVA.

4.2.3 X-Ray Fluorescence

The chemical composition of the various samples has been investigated by means of the multi-element technique X-Ray Fluorescence (XRF). X-ray fluorescence is a non-destructive analysis for the qualitative and semi-quantitative determination of elements with an atomic weight ≥ carbon (Z ≥ 6). X-ray fluorescence is based on the principle that an atom is irradiated by high-energetic radiation and releases an electron from a valence shell of the atom. A higher placed electron takes the vacant place and transmits element-characteristic radiation. The intensity of this radiation is a guideline for the concentration of the concerned element.

Semi-quantitative determination of the multi-element composition of three samples (extruded pellets without and with CMC, and extruded pellets without CMC after washing) has been attained in a PANalytical Axios-Max XRF spectrometer. Prior to the analysis, the three samples were milled followed by drying in an oven at 90°C. Subsequently, a suitable pellet has been generated by means of pressing about 1.5 g of the powdered sample with boric acid without binder; this assists in homogenization of the sample and it minimizes matrix effects.

4.2.4 SEM-EDX

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) is used to study the surface characteristics of various samples. High resolution images of surface topography, with excellent depth of field, are produced using a highly-focused, scanning (primary) electron beam. The primary electrons enter a surface with an energy of 0.5 – 30 kV and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample. An image of the sample surface can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. High spatial resolution is possible because the primary electron beam can be focused to a very small spot (<10 nm).

High sensitivity to topographic features on the outermost surface (< 5 nm) is achieved when using a primary electron beam with an energy of < 1 kV.
In addition to low energy secondary electrons, backscattered electrons and X-rays are generated by primary electron bombardment. The intensity of backscattered electrons can be correlated to the atomic number of the element within the sampling volume. Hence, some qualitative elemental information can be obtained. The analysis of characteristic X-rays (EDX or EDS analysis) emitted from the sample gives more quantitative elemental information. Such X-ray analysis can be confined to analytical volumes as small as 1 cubic micron.

4.2.5 Crushing strength

The robotic compression tester is an instrument for measuring the strength of particles and granules. The robotic compression tester measures the maximum crushing force of individual particles or granules. The crushing force of particles with sizes ranging from 500 μm to 5000 μm can be measured. About 40 up to 100 particles are individually placed on a 2 cm thick smooth finely polished stainless steel plate and the coordinates of each particle and size are determined by a CCD camera. Consecutively all particles at the known coordinates are crushed and the required force is measured with a quartz force transducer. The transducer is a device that uses the piezoelectric effect to measure pressure, acceleration, strain or force by converting them to an electrical charge. The sensitive transducer is suitable for measuring quasi-static and dynamic tensile and compressive forces ranging from a few mN to 100 N.

The principal result of the compression test is an average maximum crushing force and the particle size distribution. Compressive strength of particles and agglomerates is often proportional with the particle diameter, the relationship is generally in the form:

$$L = k D^n$$

where L is the crushing force, D is the particle diameter, k and n are constants depending on the material. The device is shown in Figure 15.

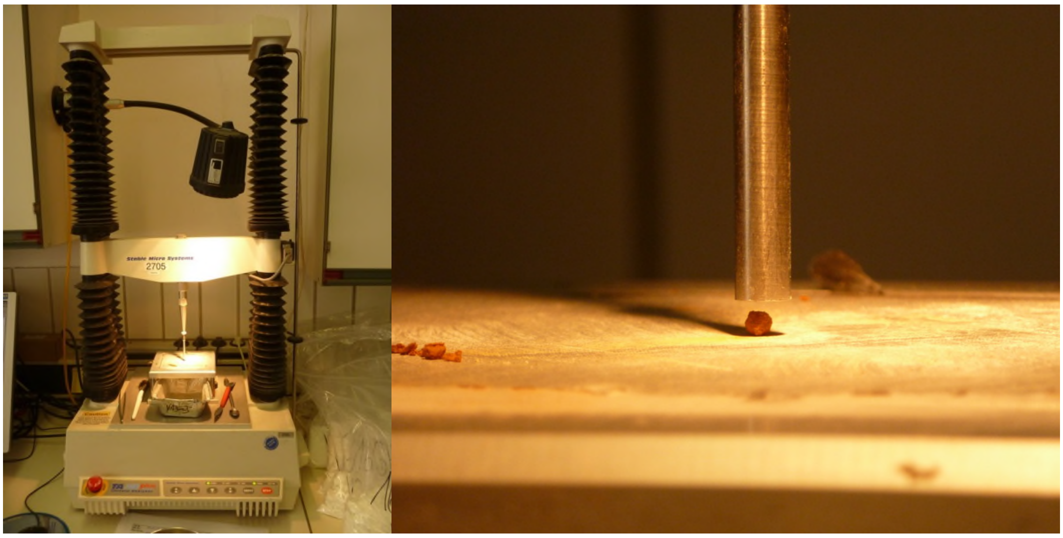


FIGURE 15: ROBOTIC COMPRESSION TESTER.

4.2.6 Iron, amorphous iron and crystalline iron determination

These analyses were carried out by a laboratory associated with Agravis. The total iron content was determined according to the analytical method AV_HeGo_001, by means of titration with $K_2Cr_2O_7$, or according to AV_HeGo-004 by means of a titration with $S_2O_4^{2-}$. In order to determine the amorphous iron AV_HeGo_005 was applied, based on a titration with $(NH_4)_2C_2O_4$ (ammonium oxalate).

4.3 Results and discussion

4.3.1 Characterization of GIH-pellets produced in laboratory

At laboratory scale GIH-pellets were produced using residuals from various sources. These include GIH-pellets based on:

- Old residual from Spannenburg
- Fresh residual from Spannenburg
- Residual from Huijbergen
- Mixture of residuals from eleven drinking water treatment facilities

Table 4 provides an overview of the chemical composition of the eleven residuals that were used to prepare GIH-pellets that can be a future product, based on drinking water residuals from the Dutch drinking water sector, production up to 1500 ton DS. It should be noted that there are large differences in the composition of these materials. Although iron is a major compound, its content varies from 31 to 53%. Other important constituents are $CaCO_3$ (2-20%) and organic materials (2.8 to 11%). The P_2O_5 content of the materials varies from 1-3.3%, which is an important parameter in determining the maximum phosphate adsorption capacity.

Although these data show that there are large differences in the sludge composition of groundwater facilities, it is yet unknown how large the variation of the individual sludges over time may be. The idea is that by using a mixture of several sludges not only sufficient material would be available, but also that a more constant general composition can be obtained.

TABLE 4: COMPOSITION OF THE MIXED IRON RESIDUAL AND OF ITS COMPONENTS ACCORDING TO ICPMS (DS = DRY SOLIDS) (ANALYSES CARRIED OUT BY OMEGAM LABORATORIES AT THE REQUEST OF AQUAMINERALS)

	Ds (%)	Production Ton D	Mix comp. %	Al %	Ca %	Fe %	Mg %	Mn %	Org.compon %	P_2O_5 %	FeO(OH) %	$CaCO_3$ %
Ossendrecht	11.5	75.9	4.9	0.14	0.63	53	0.05	0.07	3.5	1.0	84.8	2
Hoogeveen	19.7	283.7	18.4	0.01	1	49	0.07	0.19	2.8	1.9	78.4	3
Huijbergen	5.8	31.3	2.0	0.03	2.9	44	0.05	0.43	6.9	3.7	70.4	7
Oldeholtpade	1.8	30.6	2.0	0.02	3.6	43	0.10	0.34	7.3	2.6	68.8	9
Roosendaal	4.5	37.8	2.5	0.01	3.1	40	0.06	0.10	4.9	3.3	64.0	8
Noordbergum	9.2	368.0	23.9	0.02	5.7	36	0.06	0.36	4.2	3.0	57.6	14
St. Jansklooster	8.3	207.5	13.5	0.08	7.8	34	0.19	0.11	11	1.6	54.4	20
Witharen	10.8	129.6	8.4	0.05	6	34	0.09	0.15	10	1.7	54.4	15
Bergen op Zoom	4.5	54.0	3.5	0.12	4.6	33	0.06	0.39	3.4	1.9	52.8	12
Nuland	4.8	51.8	3.4	0.03	4	33	0.08	4.20	11	2.2	52.8	10
Spannenburg	4.5	270.0	17.5	0.01	7.4	31	0.13	0.18	6.5	2.5	49.6	19
Mixture		1540	100.0	0.04	4.9	38	0.10	0.36	6	2.2	61.0	12

XRD only gives qualitative information on the presence of crystals, which aren't necessarily iron oxides. By means of redox titrations more quantitative information on the presence of iron oxide crystals can be obtained. The data thus obtained are shown in Table 5. As expected the “old” Spannenburg material contained some crystallized iron oxide. However, also the “fresh” material contained such crystals, which was not in accordance with the XRD information obtained in the previous project (Hofman-Caris et al., 2015). Furthermore, it also was found that the S_{BET} value had decreased for the Spannenburg material, when compared to the data in the previous project, which may also point to partly crystallization. The explanation may be that this material had been in stock for about one year, and thus may have crystallized in the meantime. This also is in accordance with the data for the new Spannenburg sample with polymer, which was obtained directly from the plant, and didn't show the presence of crystallized iron oxides. Also in the mixed sample only a low iron oxide crystal content can be observed. For adsorption purposes this is important information, as it is known that crystalline iron oxide has a low phosphate adsorption capacity {Noijen, 1984 #883}{STOWA, 1994 #884}.

The sum of crystallized and amorphous iron is not identical to the total iron content, as in the total iron content also the insoluble iron containing compounds are taken into account, whereas amorphous and crystalline iron oxides only are determined in aqueous solution.

TABLE 5: CHARACTERIZATION OF GIH-PELLETS BY REDOX TITRATION.

Sample	Dry material content (%)	Total Fe-content (%)	Part amorphous Fe in total Fe (%)	Part crystalline Fe in total Fe (%)	BET surface (m^2/g)
GIH Spannenburg old residual	95.79	35.61	38.07	12.66	107.54
GIH Spannenburg fresh residual	94.83	40.38	44.39	11.90	152.09
GIH Mixed residuals	95.10	46.19	72.43	2.16	145.72
GIH Spannenburg + polymer*)	97.13	36.70	82.59	0.00	83.31

*) Material used for pellets made by means of extrusion. This was Spannenburg material, containing some aged sludge, to which polyacrylamide had been added for dewatering purposes.

TABLE 6: PHYSICAL CHARACTERIZATION OF GIH-PELLETS AND FERROSORP PLUS BY N_2 ADSORPTION.

sample	Weight loss (%)*)	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	V_{micro} (cm^3/g)	S_{meso} (m^2/g)
GIH Spannenburg old residual	9.7	154	0.241	0.045	63
GIH Spannenburg fresh residual	12.1	187	0.318	0.057	71
GIH Huijbergen residual	11.1	235	0.258	0.087	69
GIH Mixed residuals	1.8**	182	0.238	0.05	82
Ferrosorp Plus	10.4	216	0.597	0.017	177

*) The dry solids content thus is 100- weight loss.**) weight loss was lower because the sample was dried over a longer period of time.

The physical characterization of the GIH-pellets and Ferrosorp Plus is shown in Table 6.

Nitrogen adsorption, used to determine S_{BET}, also indicates the fraction of the space within a particle occupied by micro-pores, meso-pores and macro-pores. It was observed that the Huijbergen and Spannenburg were meso-porous, and that Ferrosorp had a relatively high content of macro-pores. Huijbergen material has many micropores, resulting in a large specific surface area. The large surface area of Ferrosorp Plus probably was caused by external surface and/or the surface area of the meso-pores (10-100 nm, maximum at 35 nm). The Huijbergen material also differs from the other material because it contains only amorphous material, whereas the other samples also contained crystalline material, mainly calcite, but, in case of Spannenburg, also silica. However, according to XRD none of these samples contained crystalline iron (this is in accordance with the redox titration results, taking into account that the Spannenburg fresh material may have aged, and thus crystallized, during storage). The chemical composition of the materials, according to X-ray fluorescence, is shown in Table 7. The samples were first washed with Milli-Q water, and then dried at 105 °C.

TABLE 7: SEMI-QUANTITATIVE COMPOSITION OF SLUDGES ACCORDING TO X-RAY FLUORESCENCE *)

Compound	Spannenburg old	Spannenburg fresh	Spannenburg with polymer**)	Huijbergen	Mixture	Ferrosorp Plus
Fe_2O_3	67.9	73.5		85.7	85.1	71.8
	69.0	*74.1*	*72.4*		*79.5*	
SiO_2	13.0	11.2		5.4	5.1	13.0
CaO	14.2	10.7		4.8	6.6	11.0
	21.2	*16.4*	*16.5*		*10.8*	
P_2O_5	2.9	3.2		3.0	1.6	1.1
MnO	0.7	0.4		0.6	0.8	1.4
SO_3	0.3	0.3		0.2	--	0.2
Na_2O	0.4	0.3		0.1	0.2	--
MgO	0.2	0.2		--	0.1	1.0
Al_2O_3	0.2	--		--	--	0.3
BaO	--	--		--	--	0.1

*) Elements with Mw> C); contents in wt%. Elements present in concentrations << 0.1 wt% have not been included. analysis carried out by DSS, data in italitcs obtained by Agravis (analysis at Hego biotec.

**) Material used for pellets made by means of extrusion. This was Spannenburg material, containing some old sludge, to which polyacrylamide had been added for dewatering purposes.

It can be observed that there are some small differences between the analytical data from DSS and Agravis for the same samples.

When the characterization data and the adsorption performance were evaluated, it was observed that the iron content of the material is a crucial parameter for the adsorption capacity of the pellets. Furthermore, the surface area available for adsorption appeared to be an important factor.

4.3.2 Characterization of sludge from Hannover

As in Germany Agravis disposes of a large amount of sludge from the drinking water facility of Hannover, it was decided to analyse this material too. However, this appeared to be very old sludge, with a relatively high content of crystalline material. As it is known that amorphous material has a significantly higher adsorption capacity for e.g. phosphate, it was decided not to continue research with this material. The characterization is shown in Table 8, in which the data are compared with previous data from Spannenburg (amorphous ironoxide) and Karlingen (partly crystalline material) (Hofman-Caris et al., 2015).

TABLE 8: CHARACTERIZATION OF SLUDGE FROM HANNOVER, COMPARED WITH PREVIOUS MATERIAL FROM SPANNENBURG AND KRALINGEN ((HOFMAN-CARIS, SIEGERS ET AL. 2015).

sample	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	V_{micro} (cm^3/g)	S_{meso} (m^2/g)
Spannenburg	230	--	--	--
Spannenburg + 2% bentonite	231	0,385	0,075	84
Kralingen	117	--	--	--
Kralingen + 2% bentonite	121	0,088	0,010	98
Ferrosorp Plus	276	0,640		--
Hannover sludge	143	0,145	0,048	60

4.3.3 Characterization of GIH-pellets produced by extrusion

The GIH-pellets were made of the residual of Spannenburg, containing some polymer (polyacrylamide). These pellets were characterized both by DSS and by Agravis. Table 9 shows some data obtained by Agravis, for the pellets used in the Waternet pilot on phosphate adsorption.

TABLE 9: ANALYSES OF EXTRUDED IRON PELLETS, USED IN THE WATERNET PILOT EXPERIMENT, BY LABOR WESSLING

Parameter	unit	%	method
DM (dry material)	%	74.1	Extraction with aqua regia
Fe	% of pellets *)	21.7	
P	mg/kg pellets*)	6.010	
Fe content	% DS	29.3	
P	mg/kg DS	4.453	
P_2O_5	mg/kg DS	10.197	

*) pellets produced without CMC

For these pellets similar analyses were carried out as for the laboratory made pellets. The results are shown in Table 10, Table 11, Table 12, and can be compared with the results shown in Table 5, Table 6, Table 7 and Table 8 respectively.

TABLE 10: COMPOSITION OF GIH-PELLETS ACCORDING TO AGRAVIS

Sludge	Dry matter (%)	Total Fe (%)	% amorphous Fe in total Fe	% crystalline Fe in total Fe	S_{BET} (m^2/g)
No CMC Treated*)	93.53	35.57	89.34	0.00	116.25
No CMC	75.75	33.58	80.72	0.00	174.13
With CMC	67.74	35.81	92.95	0.00	231.15

*) This material was washed and dried before analysis. Both other samples were analyzed without this treatment.

It can be concluded that the composition of laboratory made pellets and extruded pellets is similar, but that the specific surface may differ significantly. It is not clear what exactly causes these differences. It is to be expected that the surface area of pellets made under high pressure is lower than of pellets made at normal pressures, but this doesn't explain the relatively low S_{BET} found for the Spannenburg material with polymer, pelletized at the laboratory, nor the large differences in S_{BET} found for the extruded pellets (Table 10).

The physical parameters of the extruded pellets also were determined, and compared with data obtained for laboratory pellets (Huijbergen and mixture; determined by Agravis on 11-12-'15) (Table 11). There appears to be a good accordance between the data generated by DSS and the data from Agravis. Furthermore, it can be concluded that the S_{BET} of the extruded pellets is relatively low, which seems to be caused by the decreased pore volume of the material due to pressure.

TABLE 11: PHYSICAL PARAMETERS OF SOME SAMPLES, DETERMINED BY AGRAVIS

sample	**Weight loss (%)*)**	**S_{BET} (m^2/g)**	**V_{pore} (cm^3/g)**	**V_{micro} (cm^3/g)**	**S_{meso} (m^2/g)**
Extruded pellets	1.9	166	0.187	0.045	74
Huijbergen	2.0	233	0.283	0.076	80
Huijbergen (According to DSS)	11.1	235	0.258	0.087	69
mixture	1.8	182	0.238	0.050	82

The composition of the pellets also was determined by means of X-ray fluorescence as shown in Table 12 (compare with Table 7.

TABLE 12: COMPOSITION OF PELLETS ACCORDING TO X-RAY FLUORESCENCE, DETERMINED BY AGRAVIS

sample	**% Fe_2O_3**	**% CaO**
Extruded pellets without CMC (washed)	72.5	17.6
Extruded pellets with CMC	72.0	17.5
Extruded pellets without CMC	71.5	18.0

Obviously, the presence of CMC nor washing of the samples prior to analysis affects the Fe_2O_3 or CaO content.

Pictures and scanning electron micrographs of the materials are shown in Appendix V.

4.3.4 Characterization of pellets made by means of a rotating disk process ("build-up pelletization process").

The maximum crushing strength (N) was determined for pellets made with either cement or water glass, as shown in Table 13 and Table 14.

TABLE 13: CRUSHING STRENGTH (N) OF CEMENT BASED MATERIAL (DETERMINED BY AGRAVIS)

Sample	1 wt% cement	5 wt% cement
Drying time (days)		
7	1.70	2.06
14	2.34	2.48
21	2.42	1.72
28	4.28	2.83

TABLE 14: MAXIMUM CRUSHING STRENGTH OF WATER GLASS BASED MATERIAL (N) AFTER DRYING AT 110 °C (MEASURED BY AGRAVIS)

Sample	Crushing strength (N)
1 wt% water glass	2.26
5 wt% water glass	2.99

It is clear that drying of the cement containing pellets requires some time: during four weeks the strength appears to increase. This means that, if such pellets would have to be produced on a larger scale, a large storage facility would be required. For the water glass containing pellets drying takes place at a higher temperature, and thus these pellets don't have this disadvantage. However, their maximum strength is significantly lower. Furthermore, the pellets containing 1 wt% of cement show a higher strength in the end, although in the beginning the strength of pellets containing 5 wt% seems to be higher.

4.3.5 Surface analysis of (loaded) pellets

These analyses were carried out using SEM-EDX (Turkey) (see section 4.2.4).

On several spots on the surface of the material, as seen in scanning electron micrographs, an analysis of the elements present was carried out. Detailed information can be found in Appendix VII.

SEM-EDX experiments were carried out, using the following materials: laboratory pellets made of material from Huijbergen, from Spannenburg (material with polyacrylamide, and aged material), and from a mixture of sludges. Furthermore, pellets from Agravis (pellets made from Spannenburg with flocculant but without CMC; not crushed), and from Ferrosorp also were analyzed. The Agravis pellets also were analyzed after phosphate adsorption experiments at the laboratory, thus containing a "high" phosphate content.

The surface composition (in atom %) is shown in Table 15. For all samples different areas at the surface were analyzed, the results of which are shown in this table. It can be concluded that the surface of the material is very inhomogeneous. In that respect no differences can be observed between all samples, as the differences in area composition of one sample already are just as large as the differences between different samples. Furthermore, there also doesn’t seem to be more phosphorous present at the surface of the Agravis material, loaded with phosphorous. This may be due to the inhomogeneous nature of the material, but also may be explained by the adsorption of phosphorous inside pores, which were not taken into account in this analysis.

TABLE 15: SURFACE COMPOSITION (ATOM %) ACCORDING TO SEM-EDX

	Area	O	Fe	C	Si	Ca	P	S	Mn	Al	Na	Cl	N	Mg	F
Huijbergen	1	76.16	8.81	12.23	1.02	1.24	0.55								
		± 6.0	± 0.6	± 0.9	± 0.1	± 0.1	± 0.1								
	2	77.03	7.97	11.54	1.36	1.18	0.61	0.07	0.25						
		± 6.7	± 0.6	± 1.0	± 0.1	± 0.1	± 0.1	± 0.0	± 0.1						
	3	21.74	62.72	9.76	1.91	2.28	0.95	0.12	0.53						
		± 1.2	± 4.5	± 0.7	± 0.1	± 0.1	± 0.1	± 0.0	± 0.1						
Mixture	1	78.70	4.29	14.99	0.86	0.71	0.30		0.15						
		± 22.7	± 0.4	± 3.9	± 0.1	± 0.1	± 0.0		± 0.1						
	2	78.51	5.12	14.26	0.92	0.88	0.31								
		± 22.4	± 0.5	± 3.7	± 0.1	± 0.1	± 0.0								
	3	19.16	54.60	10.96	3.35	6.59	1.51		1.16	0.12	0.06		2.50		
		± 1.1	± 1.3	± 0.6	± 0.1	± 0.2	± 0.1		± 0.1	± 0.0	± 0.0		± 0.7		
Spannenburg (aged)	1	59.20	21.08	9.20	4.15	3.64	1.08	0.10	0.39		0.77			0.41	
		± 3.8	± 1.1	± 0.6	± 0.2	± 0.2	± 0.1	± 0.0	± 0.1		± 0.1			± 0.0	
	2	58.65	21.95	8.78	4.19	3.55	1.17	0.16	0.49		0.63			0.43	
		± 4.1	± 1.2	± 0.7	± 0.2	± 0.2	± 0.1	± 0.0	± 0.1		± 0.1			± 0.1	
	3	78.2	0.19	17.57	1.01	0.71	0.25			0.32	1.16			0.57	
		± 24.7	± 0.1	± 4.7	± 0.1	± 0.1	± 0.0			± 0.1	± 0.1			± 0.1	
	4	35.76		8.76	1.30	1.07	0.34			0.44	1.70			0.82	49.8
		± 10.4		± 2.4	± 0.1	± 0.1	± 0.1			± 0.1	± 0.2			± 0.1	± 17.2
	5	80.38	1.11	16.55	0.93	0.77	0.25								
		± 25.0	± 0.2	± 4.3	± 0.1	± 0.1	± 0.0								
Spannenburg (with polyacrylamide)	1	79.67	0.00	15.96	1.01	0.24	0.24			0.63	2.24				
		± 25.3	± 0.0	± 4.3	± 0.1	± 0.1	± 0.0			± 0.1	± 0.2				
	2	80.43		15.16	1.02	0.25	0.24			0.64	2.27				
		± 25.5		± 4.1	± 0.1	± 0.1	± 0.0			± 0.1	± 0.3				
	3	68.68	10.75	9.98	3.40	3.02	0.85	0.10	0.28	0.45	1.76	0.15		0.58	
		± 5.5	± 0.7	± 1.0	± 0.2	± 0.2	± 0.1	± 0.0	± 0.1	± 0.1	± 0.1	± 0.0		± 0.1	
	4	70.56	9.57	9.82	3.39	2.46	0.81	0.06		0.50	2.01	0.13		0.68	
		± 5.8	± 0.6	± 1.0	± 0.2	± 0.2	± 0.1	± 0.0		± 0.1	± 0.2	± 0.0		± 0.1	

	Area	O	Fe	C	Si	Ca	P	S	Mn	Al	Na	Cl	N	Mg	F
Agravis	1	61.87	19.80	9.98	3.12	3.78	0.94	0.12	0.36	0.03					
		± 4.4	± 1.1	± 0.7	± 0.2	± 0.2	± 0.1	± 0.0	± 0.1	± 0.0					
	2	60.66	21.57	8.99	3.27	3.96	1.04		0.46					0.05	
		± 4.3	± 1.2	± 0.6	± 0.2	± 0.2	± 0.1		± 0.1					± 0.0	
	3	56.72	10.59	27.60	1.77	2.48	0.56		0.23	0.02				0.03	
		± 5.3	± 0.8	± 2.1	± 0.1	± 0.2	± 0.1		± 0.1	± 0.0				± 0.0	
Ferrosorp	1	78.20	0.19	17.57	1.01	0.71	0.25			0.32	1.16			0.57	
		± 24.7	± 0.1	± 4.7	± 0.1	± 0.1	± 0.0			± 0.1	± 0.1			± 0.1	
	2	35.76		8.76	1.30	1.07	0.34			0.44	1.70			0.82	49.80
		± 10.4		± 2.4	± 0.1	± 0.1	± 0.1			± 0.1	± 0.2			± 0.1	± 17.2
	3	80.38	1.11	16.55	0.93	0.77	0.25								
		± 25.0	± 0.2	± 4.3	± 0.1	± 0.1	± 0.0								

4.3.6 Analysis of phosphorous loaded pellets

Labor Agrolab applied ISO 11885 method to determine the phosphate content of pellets used in the pilot of Amsterdam, and in this case indeed an increase in phosphorous concentration could be observed (Table 16).

TABLE 16: PHOSPHOROUS LOAD OF PELLETS

		Without CMC		With CMC
		Start	End	End
Dry matter	%	75.60	61.50	62.50
TOC	% DS	6.48	5.37	5.44
Total P_2O_5	mg/kg DS	14600	27600	27200
Orthophosphate P_2O_5	mg/kg DS	<6600	8900	8600
Water soluble phosphate P_2O_5	mg/kg DS	<1300	<1600	<1600

From these results it can be concluded that indeed the phosphorous content of the material increased by the adsorption, largely representing orthophosphate (but also other phosphate). No significant difference between both types of pellets can be observed. Also X-ray analysis was performed, giving the results shown in Figure 16.

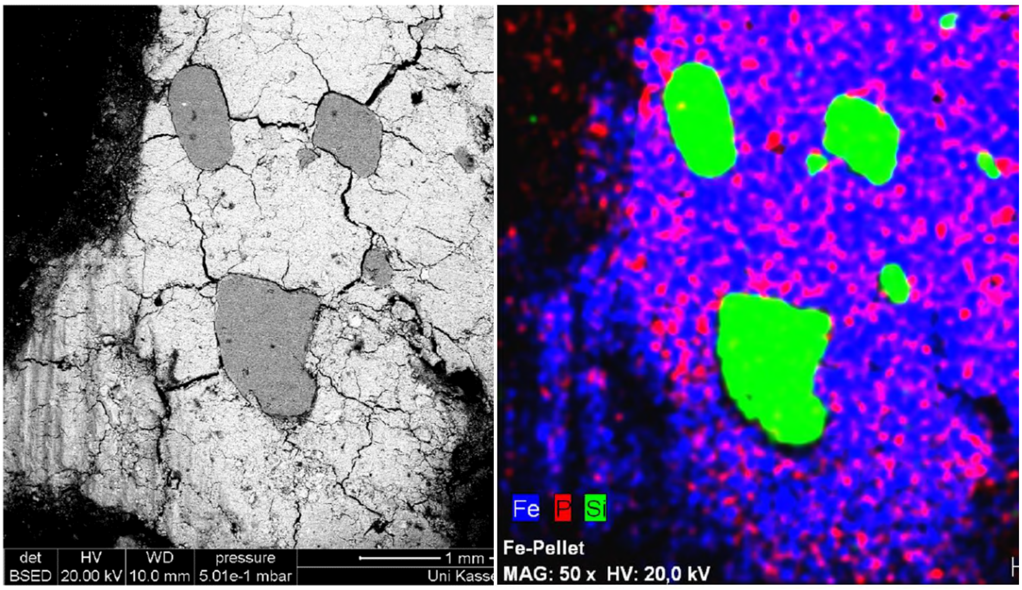


FIGURE 16: X-RAY ANALYSIS OF LOADED IRON PELLETS. RED PARTS INDICATE THE PRESENCE OF PHOSPHOROUS

The large spots represent quarz crystals. From these data it can be concluded that the phosphorous is equally distributed over the whole pellet surface.

4.4 Discussion

From the previous sections it can be concluded that there are many ways to chemically and physically characterize GIH pellets. Even if the same parameter is analyzed, differences may be obtained due to differences in the laboratories carrying out the analysis (e.g. S_{BET} and porosity), application of different methods, or differences between various batches of the same material. This has to be kept in mind while interpreting the results obtained.

Although both wet analysis and XRD give information on the presence of crystalline structures within the material, the information obtained by means of XRD is has a more qualitative character. The same can be concluded from XRF analysis, which also has a semi-qualitative character. For comparison such analyses can be carried out, but not in order to obtain absolute values.

The composition of sludge may vary as a function of place and time. Besides, due to its inhomogeneous character (containing other materials like organic matter, twigs, stones, calcite crystals, etc.), even within one batch pellets may differ from each other. It also is very likely that during the pelletization process differences between the bulk composition and the surface composition of pellets may occur. Finally, upon aging differences may occur, e.g. due to crystallization of iron oxides. Apart from these factors, which all refer to differences in the sludge material itself, also differences may occur depending on the drying and pelletization processes applied. The temperature applied may influence the DS content, crystallization and possibly the presence of organic matter. If a binder is used, the way of application and mixing of the binder may influence the effectiveness of the binder, the (surface) composition of the pellets, and thus their mechanical and adsorption properties. All these parameters should be taken into account while comparing different GIH pellets.

For commercial applications it will be very important to clearly define the pellet properties required, and how these should be determined. One of the important characteristics undoubtedly will be (mechanic) stability of the pellets, as this will affect transport and handling of the material. Determining the crushing strength may not be the optimal analytical technique, as differences between some types of pellets were found to be small, although in laboratory handling these pellets clearly behaved differently, whereas later, during pilot research, some other effect were observed. It therefore can be argued that maybe another stability test should be used to standardize pellet properties.

Finally, it can be concluded that the composition (e.eg. iron content and crystallinity) of sludges from various drinking water facilities can vary strongly. In order to obtain a “constant” composition, mixtures of a broad range of sludges can be applied. This will not only level off differences between various batches of sludge, but also ensure continuous availability of the material. According to this research, such mixed material can have very good and useful properties.

4.5 Conclusions

There are several ways to characterize iron sludges. Physical parameters like porosity and specific surface area may be important for the adsorption capacity, and thus for the applicability of GIH-pellets made out of these sludges. However, also the chemical composition may play a very important role. It was observed that relatively large differences exist between various sludges. Another aspect that may play a role is the crystallinity of the material, as it is known that goethite, an iron oxide crystal that is formed during storage or heating of the material to high temperatures, negatively affects the adsorption capacity for phosphate, and possibly also for other compounds. Besides, the surface composition of the material may be very inhomogenic, a fact which also may affect adsorption processes and adsorption capacity.

For commercial pellets it will be very important to clearly define the desired pellet properties, and how these properties should be determined.

5 Phosphate adsorption on laboratory scale

5.1 Introduction

Laboratory scale kinetics and isotherm experiments were carried out at KWR Water cycle Research Institute in the Netherlands. The objective of lab-scale orthophosphate adsorption experiments was to determine the influence of the quality of the drinking water treatment residuals on the kinetics and equilibrium of orthophosphate adsorption. Furthermore, the adsorption performance was compared with the performance of Ferrosorp Plus, an established commercial adsorbent.

5.2 Materials and methods

5.2.1 Adsorbents

Four adsorbents were used to study the sorption of orthophosphate in the laboratory. Three of them were GIH-pellets produced from the drinking water treatment residuals and the fourth one was Ferrosorp Plus (N.B. at the time these experiments were carried out it had not yet been decided that a mixed material would be beneficial, and thus only individual sludges were tested here). The GIH pellets were produced in the laboratory of KWR, according to the procedure described in chapter 3. Ferrosorp Plus was supplied by HeGo Biotech GmbH. The adsorbents (including their grain sizes) were used in the adsorption experiments:

1. GIH pellets produced from Spannenburg old sludge (grain size 0.43-2.0 mm)
2. GIH pellets produced from Spanneburg fresh sludge (grain size 0.43-2.0 mm)
3. GIH pellets produced from Huijbergen sludge (grain size 0.43-2.0 mm)
4. Ferrosorp Plus (grain size 0.5-2.0 mm)

All adsorbents were pre-treated before the start of experiments in order to remove the fines from the samples and to equalize the moisture content. Pre-treatment included washing of the adsorbents with Milli-Q water and subsequent drying at 105°C for at least 24 h.

5.2.2 Initial solution

All the adsorption experiments were conducted with an initial solution that was prepared by spiking the tap water of Halsteren (Evides) with 52.4 mg/L of ortho-PO_4. Water of Halsteren was used because it has a typical pH value for drinking water companies (as involved in this project), and a negligible arsenic concentration. Thus, the presence of arsenate cannot interfere with phosphate adsorption. Appendix IV provides an overview of the tap water quality of Halsteren. For spiking, a stock solution prepared by dissolving sodium hydrogen phosphate (Na_2HPO_4) in Milli-Q water was used. Calcium ions were removed from the tap water of Halsteren by cation exchange resins (Lewatit Monoplus S100) in order to prevent precipitation of calcium phosphate in the initial solution prior to ortho-PO_4 spiking.

5.2.3 Kinetic study

In the adsorption kinetic experiments 3 g/L of each adsorbent was dosed in 300 mL of the initial solution. The suspensions were placed in an incubator at 15 °C and mixed at 200 rpm using magnetic stirrers. Samples were collected from the glass bottles after 1 h, 3 h, 5 h, 8 h, 24 h, 48 h, 72 h and 144 h of reaction time. All the samples were immediately filtered through 0.45 µm filters. The filtered samples were analysed in the laboratory of KWR using Hach-Lange phosphate test kits.

5.2.4 Adsorption isotherms

For the adsorption isotherms an equilibration time of 72 h was applied, though later it was found that real equilibrium was not achieved in this period. The dose of sorbents was varied (1 g/L, 2 g/L, 3 g/L, 4 g/L and 5 g/L) and the orthophosphate concentration was kept constant at 52.4 mg/L. The suspensions were placed in an incubator at 15 °C and mixed at 200 rpm using magnetic stirrers. After 72 h the samples were filtered through 0.45 µm filters and analysed in the laboratory of KWR using Hach-Lange phosphate test kits.

5.3 Results and discussion

5.3.1 Adsorption kinetics

Figure 17 shows the uptake of orthophosphate by the four sorbents as a function of time. It can be observed that the adsorption continued between the last two sampling events for all the adsorbents, therefore it is not certain whether the adsorption equilibrium had been reached by the time the experiments were terminated.

In Figure 17 it can be observed that the uptake of orthophosphate was the highest in case of GIH-pellets produced from the Huijbergen residual and the lowest in case of the GIH-pellets produced from the Spannenburg old residual. The GIH pellets produced from the fresh residual of Spannenburg showed a slightly higher uptake of orthophosphate compared to Ferrosorp Plus, though the uptake by both these adsorbents is of the same order of magnitude.

The adsorption performance shown in Figure 17 can partly be explained based on the characterization results presented in chapter 4. The GIH-pellets produced from Huijbergen residual showed the highest specific surface area (235 m^2/g) and iron content (85.2 % of Fe_2O_3) among all the fours adsorbents, which results in the highest phosphate uptake. The specific surface area and iron content were the lowest for the GIH-pellets that were produced from the old Spannenburg residual (154 m^2/g and 67,9%, respectively), which resulted in the lowest phosphate uptake. The iron content of the Ferrosorp Plus and the GIH-pellets produced from the fresh Spannenburg residual was comparable (73,5 and 71,8% respectively), however there was a significant difference between their specific surface areas. The specific surface area of Ferrosorp was significantly higher than that of the fresh Spannenburg material (216 and 187 m^2/g). As both materials show a similar adsorption behaviour for phosphate in this single experiment, this indicates that possibly the iron content is a more important parameter to evaluate the adsorption capacity than specific surface area.

Modelling, using an pseudo-second order kinetic model and an intra-particle diffusion model, is described in Appendix VIII.

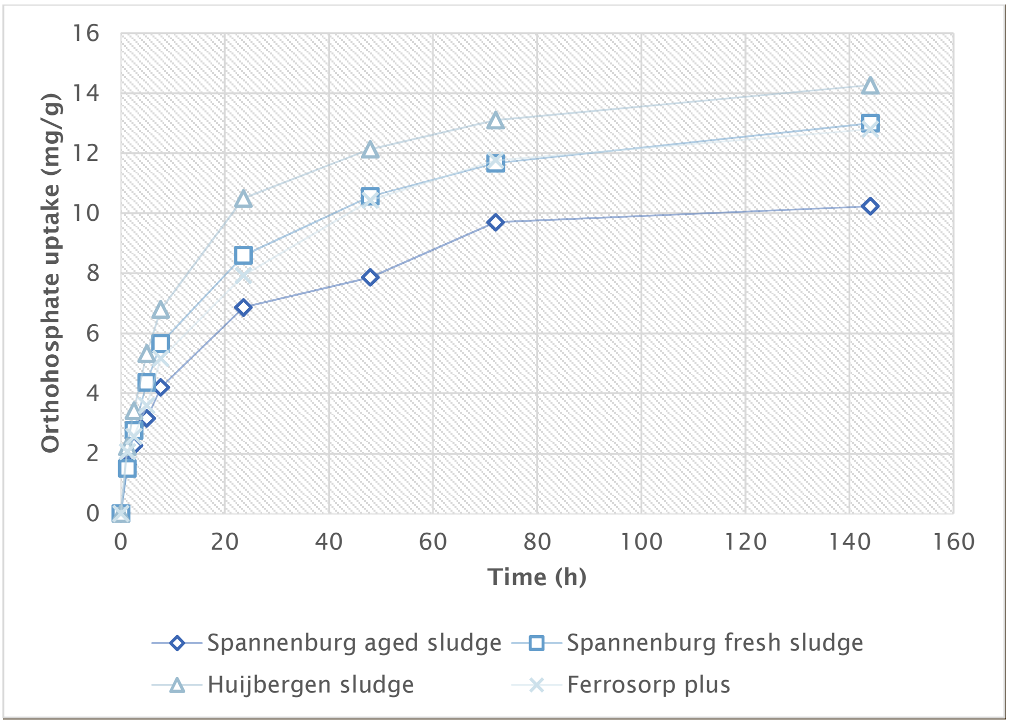


FIGURE 17 UPTAKE OF ORTHOPHOSPHATE AS A FUNCTION OF TIME.

5.3.2 Adsorption isotherms

The affinity of the solute for an adsorbent is generally evaluated by adsorption isotherms. Figure 18 shows the adsorption isotherms of orthophosphate adsorption by three types of GIH-pellets and Ferrosorp Plus at 15°C. It can be seen that the orthophosphate adsorption was highest in case of GIH-pellets produced from Huijbergen sludge and lowest in the case of Spannenburg old material. The GIH-pellets produced from fresh Spannenburg residual and Ferrosorp Plus show comparable adsorption.

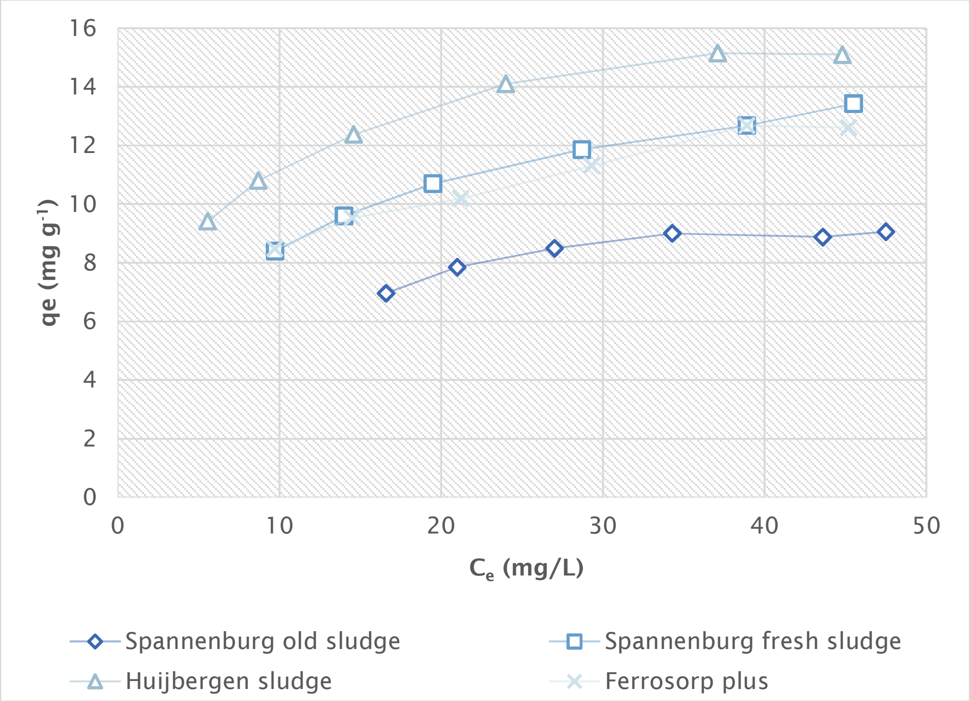


FIGURE 18 ADSORPTION ISOTHERMS OF ORTHO-PO_4 ONTO GIH PELLETS AND FERROSORP PLUS AT 15°C.

5.3.2.1 Data fitting to Freundlich and Langmuir models

In order to describe the equilibrium adsorption mathematically there are various models available, differing in complexity and the number of necessary parameters. In this study two well-known models, namely Freundlich and Langmuir, were applied to evaluate the adsorption isotherm data. The Freundlich isotherm is an empirical equation that assumes that adsorption occurs on a heterogeneous surface through a multi-layer adsorption mechanism (Fierro, Torné-Fernández et al. 2008). The Freundlich equation is:

EQUATION 5-1

$$q_e = K_F C_e^{1/n}$$

Where K_F is the Freundlich constant related to the adsorption capacity (mg g^{-1}.(mg L^{-1})^n). q_e is the adsorption capacity at equilibrium, C_e is the concentration of solute at equilibrium (mg L^{-1}) and n is the dimensionless empirical parameter representing the energetic heterogeneity of the adsorption sites (Fierro, Torné-Fernández et al. 2008).

Both K_F and n are measures of the adsorption capacity and intensity of adsorption (Malik 2004). They have to be determined empirically. At 1/n = 1 linear adsorption takes place, if 1/n<1 the adsorption process is chemical in nature, and if 1/n>1 it is cooperative.

The Langmuir isotherm accounts for surface coverage by balancing the relative rates of uptake and release. The Langmuir model assumes that the adsorbent has a limited number of adsorption sites (one layer) with similar affinity or adsorption activation energy. The solute can chemically bind to these sites, a maximum of one molecule per adsorption site. Moreover, this model assumes that there is no interaction between adsorbed molecules. The Langmuir equation is:

EQUATION 5-2

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

Where q_e and C_e have the same meaning as in the Freundlich isotherm model, q_m is the maximum sorption capacity (mg g^{-1}) and K_L is the adsorption equilibrium constant (L mg^{-1}).

The efficiency of the adsorption process can be represented by the dimensionless equilibrium parameter, commonly known as the separation factor R_L. It is represented as (Hall, Eagleton et al. 1966, Weber and Chakravorti 1974):

EQUATION 5-3

$$R_L = \frac{1}{1 + K_L C_0}$$

Where C_o is the initial solute concentration (mg L^{-1}). If $R_L>1$ adsorption is unfavorable, if R_L = 1 it is linear, if $0<R_L<1$ adsorption is favorable, and if $R_L=0$ irreversible adsorption will take place.

Table 17 and Table 18 present the coefficients of determination (R^2) and the parameters of Freundlich and Langmuir models respectively. For this single experiment it seems that both the models fit the adsorption data reasonably well. The data indicate that the Langmuir model describes the adsorption isotherms of GIH-pellets better compared to Ferrosorp Plus, which is better described by the Freundlich model. However, it is suggested to perform these experiments in duplicate to confirm this observation, as only a limited set of data was available for this modelling, and differences may not be significant. The q_m values determined from the intercept of the linearized Langmuir isotherms show the following order of adsorbents based on their adsorption capacity: Huijbergen sludge>Spannenburg fresh sludge>Ferrosorp Plus>Spannenburg old sludge.

The q_e values obtained from the pseudo-second order kinetic model and the Langmuir adsorption isotherm are in the same order of magnitude, and show the same trend.

In Table 18 the values obtained for R_L are between 0 and 1. This indicates that adsorption of phosphate is favorable. Table 17 shows that the values of 1/n for all the adsorbents were <1, representing chemical adsorption of orthophosphate on all the adsorbents.

TABLE 17 FREUNDLICH ADSORPTION PARAMETERS.

Adsorbents	**R^2**	**K_F (mg/g)(mg/L)^n**	**1/n**
Spannenburg old sludge	0.862	3.81	0.232
Spanneburg fresh sludge	0.993	4.37	0.295
Huibergen sludge	0.977	6.48	0.233
Ferrosorp Plus	0.985	4.59	0.269

TABLE 18 LANGMUIR ADSORPTION PARAMETERS DERIVED FROM EXPERIMENTAL DATA (VALUES BETWEEN BRACKETS GIVE THE VALUE CALCULATED USING A PSEUDO-SECOND ORDER MODEL, SEE TABLE 32 IN APPENDIX VIII).

Adsorbents	**R^2**	**q_m (mg/g)**	**K_L (L/mg)**	**R_L**
Spannenburg old sludge	0.932	11.0 (10.7)	0.110	0.173
Spanneburg fresh sludge	0.994	15.5 (13.6)	0.119	0.160
Huibergen sludge	0.990	16.5 (14.8)	0.231	0.083
Ferrosorp Plus	0.956	14.2 (13.5)	0.144	0.132

5.4 Comparison of GIH pellets with Ferrosorp Plus

There are two significant differences between Ferrosporp Plus and the GIH pellets (made by extrusion) described in this report: the DS content and the iron content. This is shown in Table 19.

TABLE 19: COMPARISON OF Fe CONTENT IN FERROSORP PLUS AND GIH-PELLETS

Sample	**DS (%)**	**% Fe in DS**	**% Fe in total material**	**Fe dosage at 3 g pellets/L (g Fe/L)**
Ferrosorp Plus	88.9	40	35.6	1.068
GIH pellets	74.1	29.3	21.7	0.651

If the phosphate adsorption is corrected for the iron content, the adsorption capacity is in the same order of magnitude as the adsorption capacity of Ferrosorp Plus.

5.5 Conclusions and recommendation

From the content presented in this chapter the following conclusions can be drawn:

Regarding kinetics, GIH-pellets and Ferrosorp show similar adsorption trends. It was found that it takes a relatively long time to obtain equilibrium.

Regarding the adsorption equilibrium, the adsorption capacity of GIH-pellets and Ferrosorp Plus was in the similar range when the iron content was similar in both materials, despite the differences in pore volume and dimensions. The adsorption efficiency of GIH-pellets is primarily dependent on the content of iron in the drinking water treatment residuals. Higher iron concentration leads to higher adsorption at equilibrium. Specific surface area may still be an indicator of adsorption performance. Ideal would be to consider both the iron content and specific surface area if a comparison between different adsorbents has to be made, for instance by the end users.

6 Phosphate adsorption at pilot scale

6.1 Introduction

Pilot scale experiments were carried out in Amsterdam to evaluate the GIH-pellets under field conditions. In this study the GIH-pellets, that were produced at Agravis by extrusion pelletization, using (mixed old and new) residual of Spannenburg, were used for treating surface water from a canal to control eutrophication. The pilot installation was mainly operated by the process technologists at Waternet. KWR provided assistance during the start-up and shut-down of the installations.

6.2 Materials and methods

Experiments with the GIH-pellets started on Sept. 16th 2015. After some start-up problems the installation was operated continuously from Oct. 1st 2015 until March 24th 2016.The experiments took place in a container, placed in the Comeniusstraat in Amsterdam, where water from the Sloterbinnenpolder was treated. Water was pumped from a ditch and treated in a 20 ft container, in which 3 testcontainers had been installed. After treatment, the water was discharged in the same ditch, located about 10 meters from the intake point (Figure 19). The pilot set-up is shown in Figure 19.

FIGURE 19: PICTURES OF THE PILOT SET-UP AT WATERNET, AMSTERDAM.

Pellets, made from (mixed old and new) water treatment residual of Spannenburg was used and extrusion was used to pelletize the residuals after drying. More details can be found in

Chapter 3. GIH-pellets with and without CMC were used in containers. First three layers of gravel were applied:

- 20 cm gravel with grain size 16-32 mm
- 20 cm of gravel with grain size 8-16 mm
- 20 cm of gravel with grain size 4-8 mm

In tanks 1 and 2 on top of this gravel pack GIH-pellets were deposited. In tank 1 15 cm of pellets (120 L) prepared with CMC were applied, and in tank 2 the same amount of pellets prepared without CMC. Tank 3 was placed and filled in October 5th 2015, without any GIH-pellets (blank). Filling of the tanks is shown in Figure 20.

FIGURE 20: FILLING OF THE TANKS WITH GRAVEL AND IRON PELLETS

Water from the ditch was pumped into a buffer vessel, from which it was pumped through the tanks in an upflow direction, by means of a pressure pump. Previous research, in which filters with downflow operation had been applied, had shown that in that case filter blocking occurred due to contamination of the filter. In every tank the flow could be controlled by means of diaphragm valves. The effluent of the filters was discharged in the same ditch.

The process scheme is shown in Figure 21.

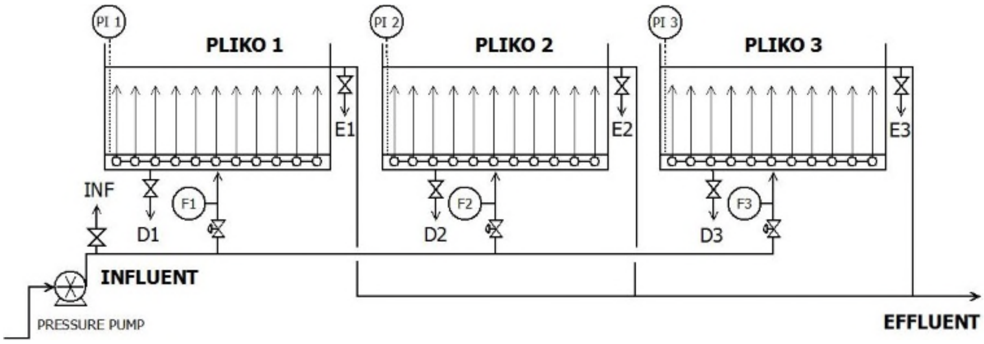


FIGURE 21: PROCESS FLOW DIAGRAM OF THE PILOT SET-UP AT THE SLOTERPLAS IN AMSTERDAM

Weekly the influent and all three effluents were sampled. Furthermore, the tanks were frequently backwashed, and the backwash water was sampled too. In order to determine the effect of the residence time the flow through the filter bed, and thus the empty bed contact time was increased twice during the experimental period (see Table 20).

TABLE 20: FLOW THROUGH THE FILTER BEDS DURING THE EXPERIMENTS (L/h)

Period	Start of period	End of period	Column 1 (with CMC)	Column 2 (no CMC)	Column 3 blank
1	16-09-2015	17-11-2015	81	74	71
2	17-11-2015	22-01-2016	128	171	108
3	22-01-2016	24-03-2016	181	193	157

The porosity of the filter beds with iron pellets is about 50%, as a result of which the filters contain about 60 L of water. In tank nr. 1 the residence time of the water was decreased from 44 to 20 minutes in two steps, whereas in tanks 2 and 3 it was decreased from 48 minutes to 19 minutes.

All the samples were analysed at HWL.

6.3 Results and discussion

During period 1 effective removal of orthophosphate was observed in tanks 1 and 2, where the phosphate content of the water decreased from 0.6 to 0.05 mg P/L, as shown in Table 21and Figure 22). The difference between influent and the effluent of tank 3 (not containing any GIH-pellets) can be explained from the increasing influent concentrations in this period, and the fact that the flow through tank 1 was started on a later date.

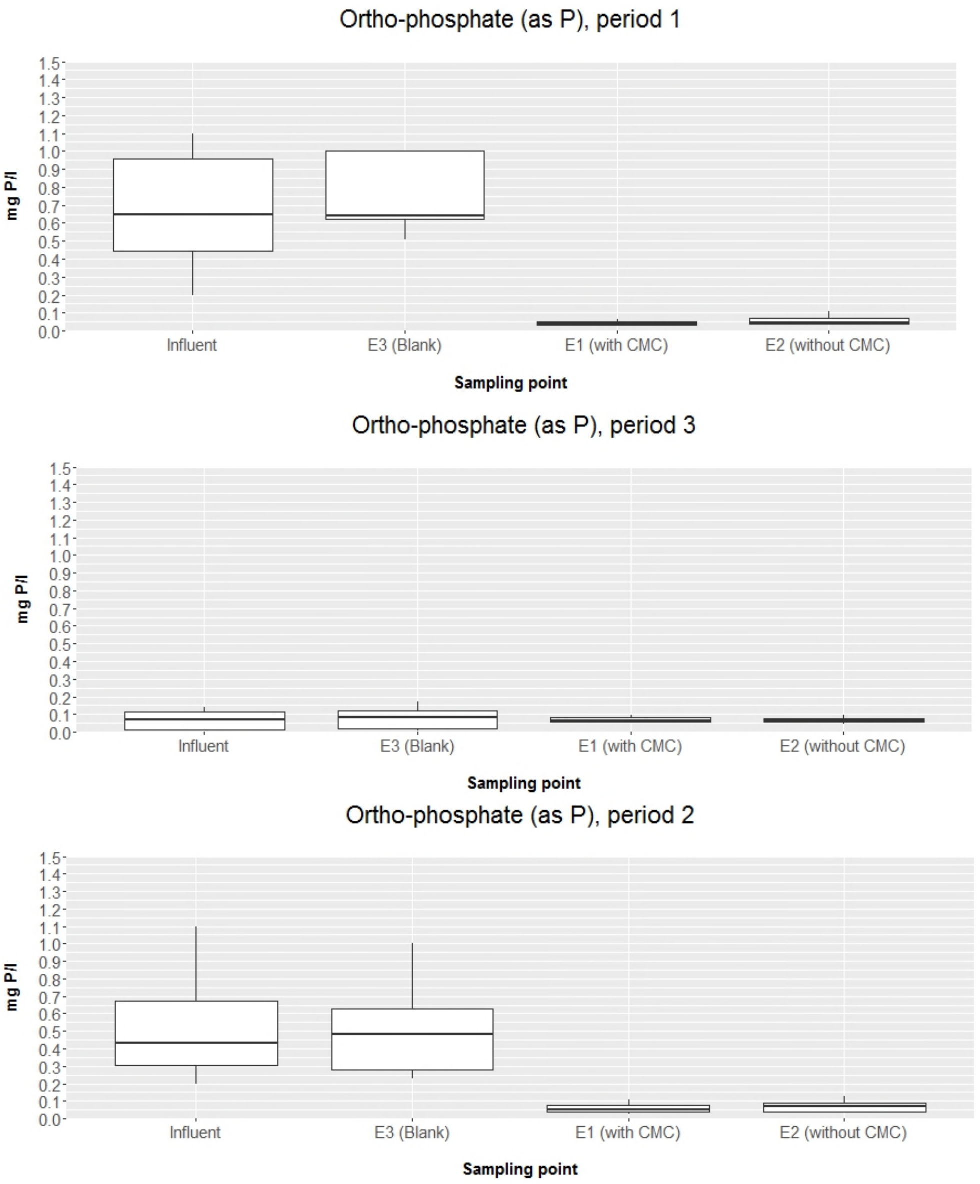


FIGURE 22: EFFECT OF FILTRATION ON ORTHOPHOSPHATE CONCENTRATIONS DURING THE PILOT TESTS. E1 = EFFLUENT FROM TANK 1 (GIH PELLETS WITH CMC); E2 = EFFLUENT FROM TANK 2 (GIH PELLETS WITHOUT CMC); E3 = EFFLUENT FROM TANK 3 (WITHOUT GIH PELLETS)

TABLE 21: ORTOPHOSPHATE CONCENTRATIONS.

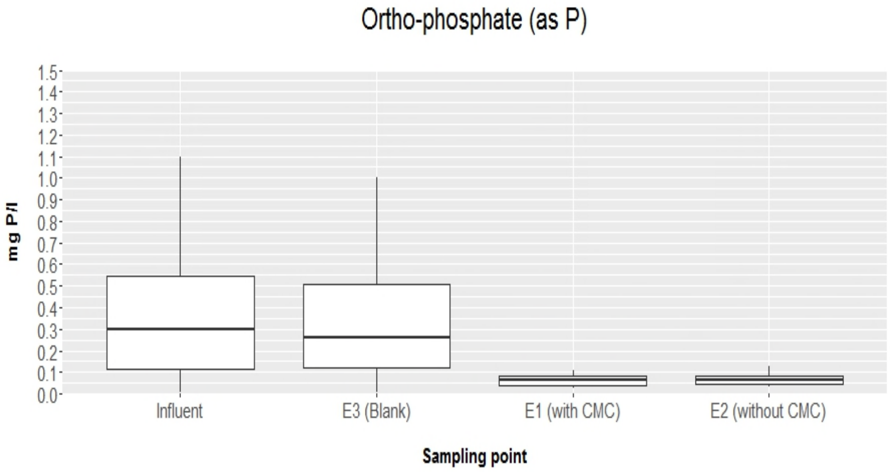
period		Influent (mg/L)	Tank 1, with CMC (mg/L)	Tank 2, no CMC (mg/L)	Tank 3 Blank, (mg/L)
1	Average conc.	0.68	0.056	0.042	0.75
	Standard deviation	0.30	0.026	0.011	0.21
	Number of samples	10	15	11	6
2	Average conc.	0.38	0.083	0.075	0.36
	Standard deviation	0.14	0.026	0.026	0.13
	Number of samples	11	10	11	12
3	Average conc.	0.068	0.067	0.072	0.079
	Standard deviation	0.050	0.018	0.014	0.056
	Number of samples	8	15	15	10

After the flow had been increased (period 2), the orthophosphate content of the effluent remained < 0,1 mg P/L, although it was higher than in period 1. In this period the influent concentrations decrease from an average of 0.6 to 0.3 mg P/L.

During the third period, early spring, the orthophosphate content decreased even further till about 0,1 mg P/L. Also in the effluent the concentrations remained on this level, showing no release of orthophosphate.

The average removal of orthophosphate over the whole period appeared to be 83% for the GIH-pellets with CMC and 82% for the pellets without CMC.

The orthophosphate concentrations in influent and effluents are shown in Figure 23.



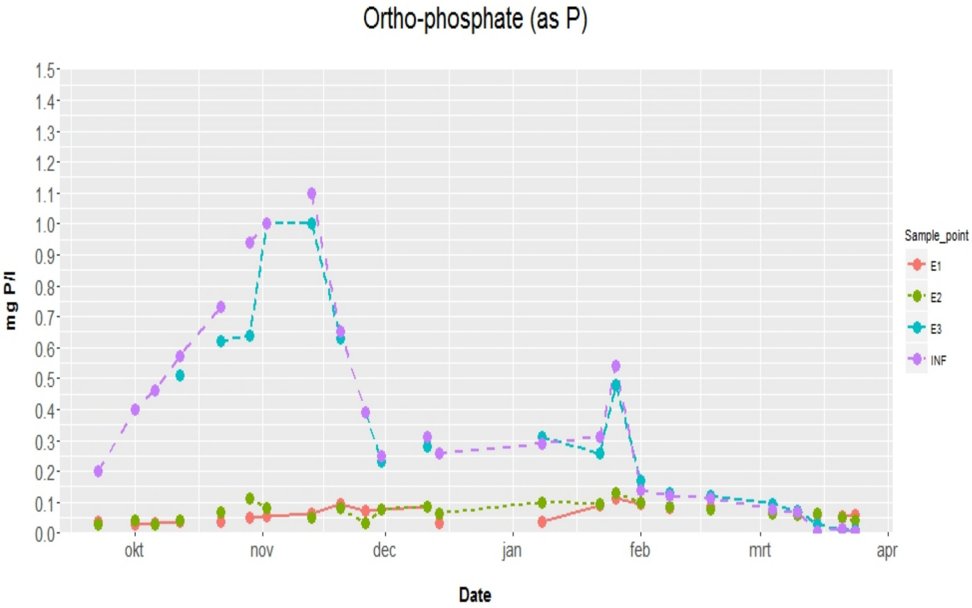


FIGURE 23: ORTHOPHOSPHATE CONCENTRATIONS IN INFLUENT AND EFFLUENTS DURING THE EXPERIMENTAL PERIOD. E1 = EFFLUENT FROM TANK 1 (GIH PELLETS WITH CMC); E2 = EFFLUENT FROM TANK 2 (GIH PELLETS WITHOUT CMC); E3 = EFFLUENT FROM TANK 3 (WITHOUT GIH PELLETS);

Also the total phosphorous concentrations were determined. Here too the removal appeared to be effective: the average effluent concentration was about 0,11 mg P/L, half of which consisted of orthophosphate. Detailed results are shown in Figure 24.

Figure 25 shows the development of total phosphorous concentrations during the experimental period.

TABLE 22: TOTAL PHOSPHOROUS CONCENTRATIONS IN INFLUENT AND EFFLUENTS

period		Influent (mg/L)	Tank 1, with CMC (mg/L)	Tank 2, no CMC (mg/L)	Tank 3 Blank (mg/L)
1	Average conc.	0.79	0.11	0.11	0.89
	Standard deviation	0.35	0.006	0.07	0.30
	Number of samples	10	15	11	6
2	Average conc.	0.55	0.19	0.15	0.48
	Standard deviation	0.21	0.07	0.05	0.18
	Number of samples	11	10	11	12
3	Average conc.	0.208	0.084	0.076	0.194
	Standard deviation	0.050	0.018	0.014	0.056
	Number of samples	8	15	15	10

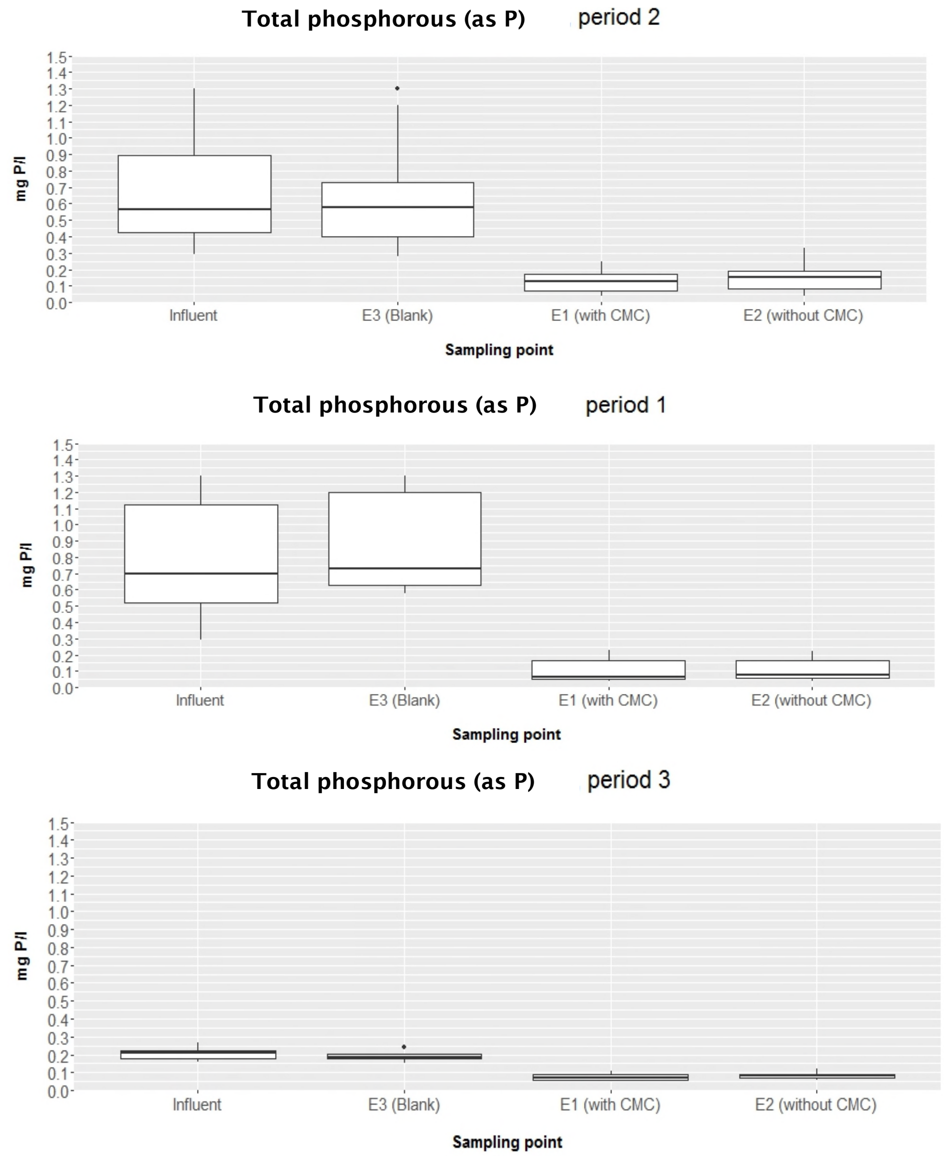
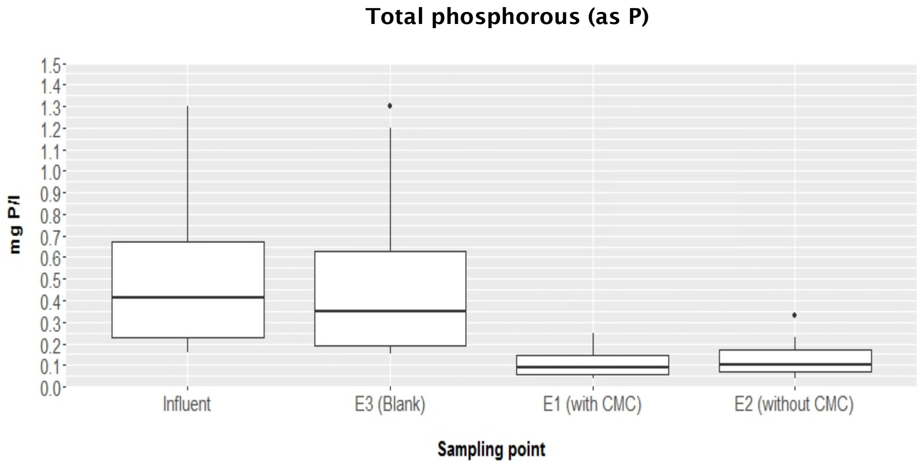


FIGURE 24: EFFECT OF FILTRATION ON TOTAL PHOSPHOROUS (P) CONCENTRATIONS DURING PERIODS 1, 2 AND 3. E1 = EFFLUENT FROM TANK 1 (GIH PELLETS WITH CMC); E2 = EFFLUENT FROM TANK 2 (GIH PELLETS WITHOUT CMC); E3 = EFFLUENT FROM TANK 3 (WITHOUT GIH PELLETS);



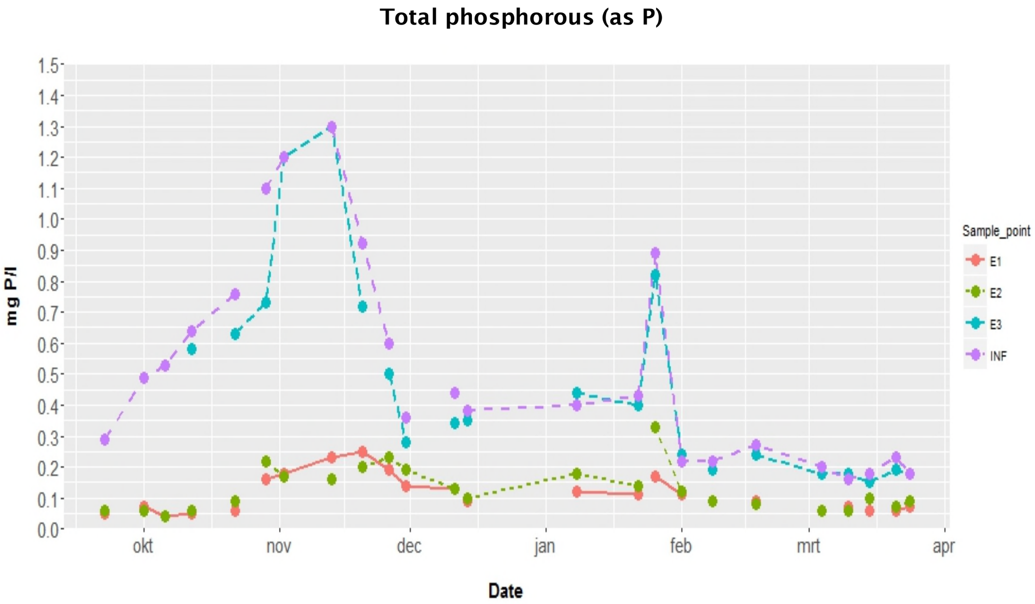


FIGURE 25: DEVELOPMENT OF TOTAL PHOSPHOROUS (AS P) CONCENTRATIONS DURING THE EXPERIMENTAL PERIOD. E1 = EFFLUENT FROM TANK 1 (GIH PELLETS WITH CMC); E2 = EFFLUENT FROM TANK 2 (GIH PELLETS WITHOUT CMC); E3 = EFFLUENT FROM TANK 3 (WITHOUT GIH PELLETS);

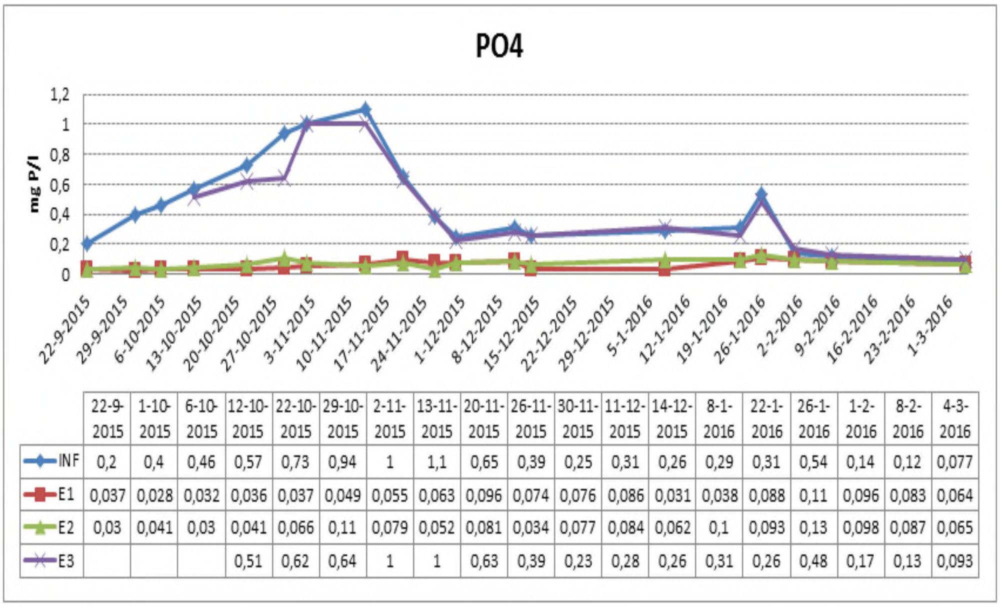
Before and after the experiments the composition of the GIH pellets was determined by Labor Agrolab. The results are shown in Table 23.

TABLE 23: COMPOSITION OF IRON PELLETS AT THE START AND END OF THE EXPERIMENTS

		Original Material (without CMC)	Tank 1 With CMC	Tank 2 Without CMC
DS	%	75.60	62.50	61.50
TOC	% DS	6.48	5.44	5.37
Total P_2O_5	mg/kg DS	14600	27200	27600
Orthophosphate (P_2O_5)	mg/kg DS	<6600	8600	8900
Water soluble phosphate (P_2O_5)	mg/kg DS	<1300	<1600	<1600

A total overview of the phosphate concentrations in influent and in all three effluents over the whole period is shown in Figure 26. This clearly shows that the phosphate concentrations in the blank effluent are identical to the influent concentrations, and that the effluent of both containers filled with GIH pellets is significantly lower, independently from the variations in the influent. The difference between pellets with and without CMC in this case appears to be negligible.

Test duration 6 month (INF – Influent / E1 und E2 - GIH Agravis / E3 – effluent, without filter)



	22-9-2015	1-10-2015	6-10-2015	12-10-2015	22-10-2015	29-10-2015	2-11-2015	13-11-2015	20-11-2015	26-11-2015	30-11-2015	11-12-2015	14-12-2015	8-1-2016	22-1-2016	26-1-2016	1-2-2016	8-2-2016	4-3-2016
INF	0,2	0,4	0,46	0,57	0,73	0,94	1	1,1	0,65	0,39	0,25	0,31	0,26	0,29	0,31	0,54	0,14	0,12	0,077
E1	0,037	0,028	0,032	0,036	0,037	0,049	0,055	0,063	0,096	0,074	0,076	0,086	0,031	0,038	0,088	0,11	0,096	0,083	0,064
E2	0,03	0,041	0,03	0,041	0,066	0,11	0,079	0,052	0,081	0,034	0,077	0,084	0,062	0,1	0,093	0,13	0,098	0,087	0,065
E3				0,51	0,62	0,64	1	1	0,63	0,39	0,23	0,28	0,26	0,31	0,26	0,48	0,17	0,13	0,093

FIGURE 26: PHOSPHATE CONCENTRATIONS IN INFLUENT AND ALL THREE EFFLUENTS DURING THE EXPERIMENTAL PERIOD. E1 = EFFLUENT FROM TANK 1 (GIH PELLETS WITH CMC); E2 = EFFLUENT FROM TANK 2 (GIH PELLETS WITHOUT CMC); E3 = EFFLUENT FROM TANK 3 (WITHOUT GIH PELLETS);

In both filters a volume of 120 L of pellets was applied with a bulk density of about 2 kg/L. For both filter beds the phosphate binding appeared to be about 5,6 g/kg dry matter (5,68 and 5,50 for tank 1 and 2 respectively). This is about 20 g/kg Fe (taking into account an iron content of 29.3% in DS (21,7% in the original material with a DS content of 74.1%), according to the analysis by Agravis). Together with the initial phosphorus content (6 – 6,4 g P/ kg Fe) the total adsorption was about 26 g P/ kg Fe. According to previous investigations (Hofman-Caris et al., 2015), the maximum phosphorous adsorption capacity of iron pellets, taking into account the initial phosphorous content, was about 45 g P/kg Fe. This refers to pellets with a higher porosity and thus a higher specific surface area, which might explain the higher value. On the other hand in this experiment full adsorption had not been reached yet, so the total adsorption capacity might even be higher than 26 g/kg.

Taking into account the different flows and differences in phosphate concentrations in the water samples, a load of 2,44 and 2,74 g/kg dry matter respectively can safely be estimated from the pilot experiments. This is about half of the load that was calculated for laboratory experiments based on the differences between the original and residual material; about 10 g/kg Fe additional P-adsorption. However, as no breakthrough of the phosphate was observed at a residence time of about 20 minutes at the end of the experimental period, this is not the maximum adsorption capacity. Furthermore, in order to correctly determine the adsorption capacity, the flow through the filters should not have been changed during the experiment.

6.4 Conclusions and recommendation

The data clearly show that application of GIH pellets for phosphate removal from surface water is an interesting possibility. It can be concluded that the water quality was significantly improved during the pilot experiments. For design purposes a maximum load of at least 4 g P/ kg dry matter can be assumed (about 20 g P/kg Fe), and a minimum residence time of 20 minutes. The data obtained are an estimate. In order to really determine the influence of kinetics, several EBCT's should be tested in separate experiments at different flows, and experiments should be carried out until breakthrough of the phosphate is obtained.

7 Arsenic adsorption on laboratory scale

7.1 Introduction

Laboratory scale kinetics and isotherm experiments were carried out at KWR Water cycle Research Institute in the Netherlands. The experiments were aimed at studying the influence of drinking water treatment plant residual quality on As adsorption by GIH-pellets. It must be noted that all the adsorption experiments were conducted with arsenate [As(V)]. The commercial Ferrosorp Plus was used for the comparison of adsorption efficiency of the GIH pellets.

7.2 Materials and methods

7.2.1 Adsorbents

Four sorbents were used to study the adsorption of As. Three of them were GIH pellets produced from drinking water treatment residuals of Dutch drinking water treatment facilities and the fourth one was Ferrosorp Plus. The GIH pellets were produced in the laboratory of KWR, according to the procedure described in section 3.1. Ferrosorp Plus was supplied by HeGo Biotech GmbH (Germany). A list of adsorbents and particle sizes used in the adsorption experiments is shown below:

1. GIH-pellets produced from Spannenburg old sludge (grain size 0.43-2.0 mm)
2. GIH-pellets produced from Spannenburg fresh sludge (grain size 0.43-2.0 mm)
3. GIH-pellets produced from Huijbergen sludge (grain size 0.43-2.0 mm)
4. Ferrosorp Plus (grain size 0.5-2.0 mm)

All the adsorbents were pre-treated before the start of experiments in order to remove the fines from the samples and to equalize the moisture content. Pre-treatment included washing of the adsorbents with Milli-Q water and subsequent drying at 105°C for at least 24 h. After the pre-treatment the moisture content in each of the adsorbents was approximately equal. See Table 6.

7.2.2 Initial solution

All the adsorption experiments were conducted with an initial solution that was prepared by spiking the tap water of Halsteren (Evides) with 100 µg/L of As. Appendix IV provides an overview of the tap water quality of Halsteren. Tap water of Halsteren was used because it contained <1 µg/L As. For spiking, a stock solution prepared from the standard As(V) solution was used. Milli-Q water was used for preparing the stock solution.

7.2.3 Kinetic study

In the adsorption kinetic experiments 0.5 g/L of each adsorbent was dosed in 300 mL of the initial solution. The suspensions were placed in an incubator at 15 °C and mixed at 200 rpm using magnetic stirrers. Samples were collected from the glass bottles after 1 h, 3 h, 5 h, 8 h, 24 h, 48 h and 72 h of reaction time. All the samples were immediately filtered through 0.45 µm filters. The filtered samples were analysed in the laboratory of KWR by means of ICP-MS.

7.2.4 Adsorption isotherms

For the sorption isotherms an equilibration time of 72 h was applied, though later it was found that within this period no real equilibrium was achieved. The dose of adsorbents was varied (0.1 g/L, 0.3 g/L, 0.5 g/L, 0.7 g/L, 1.0 g/L and 1.5 g/L) and the As concentration was kept constant at 100 µg/L. The suspensions were placed in an incubator at 15 °C and mixed at 200 rpm using magnetic stirrers. After 72 h the samples were filtered through 0.45 µm filters and analysed in the laboratory of KWR by means of ICP-MS.

7.3 Results and discussion

7.3.1 Adsorption kinetics

Figure 27shows the uptake of As by the adsorbents as a function of time. It can be observed that the uptake of As continued between the last two sampling events for all the adsorbents, and therefore it is not certain whether the adsorption equilibrium had been reached at the time the experiments were terminated. Nevertheless, it can be observed that the uptake of As was the highest in case of GIH-pellets produced from the drinking water treatment residual of Huijbergen and the lowest in case of GIH-pellets produced from the Spannenburg old residual. Ferrosorp Plus may have shown slightly higher uptake of As compared to the GIH-pellets produced from the fresh residual of Spannenburg, though the adsorption by both these adsorbents was of the same order of magnitude. These results are in line with the phosphate adsorption results, where the higher iron content and S_{BET} of Huijbergen material (85.2% and 235 m^2/g respectively) seemed to cause a higher adsorption as well, whereas the lower iron content and S_{BET} of the old Spannenburg material (67.9% and 154 m^2/g respectively) caused the lowest adsorption, and Ferrosorp Plus and fresh Spannenburg material showed similar results (Ferrosorp 73.5% Fe and 216 m^2/g, Spannenburg fresh 71.8% and 187 m^2/g).

Modelling, applying a pseudo-second order kinetic model and an intra-particle diffusion model, is shown in Appendix IX.

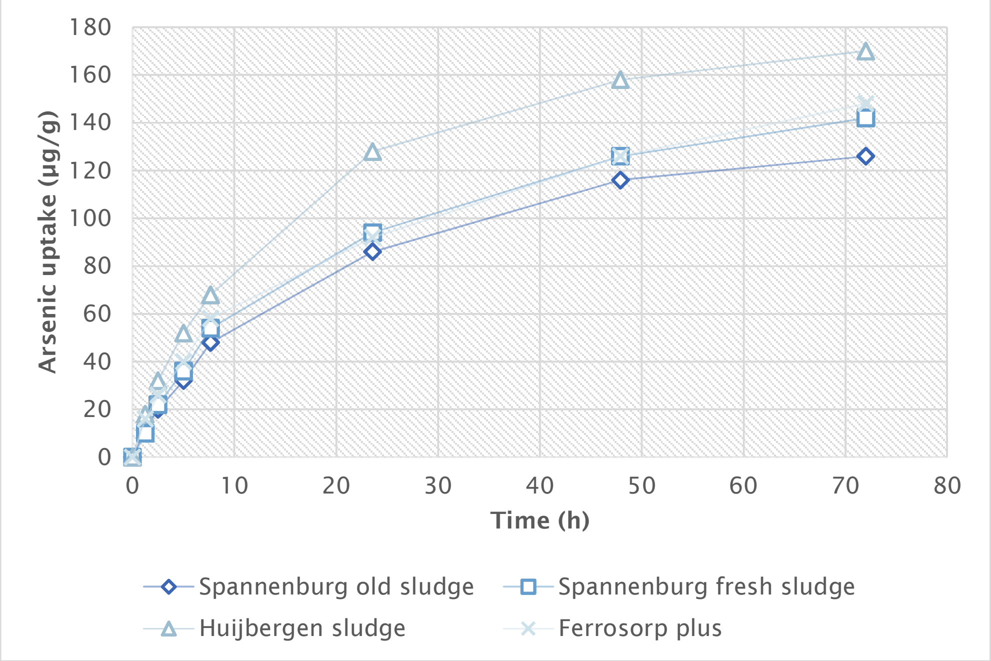


FIGURE 27 UPTAKE OF As AS A FUNCTION OF TIME.

7.3.2 Adsorption isotherms

The affinity of the solute for an adsorbent is generally evaluated by calculating adsorption isotherms.Figure 28 shows the adsorption isotherms of As at 15°C. It can be seen that the adsorption isotherms did not reach a plateau. The equilibrium adsorption capacity increases sharply with the increase in the equilibrium As concentration. This was due to the fact that a low As concentration was used in the adsorption experiments (100 µg/L). Performing the adsorption experiments in mg/L range of As concentration might have shown a less steep curve, similar to that was obtained for orthophosphate adsorption isotherm.

It can be seen that As adsorption was the highest in case of GIH-pellets produced from Huijbergen sludge and lowest in the case of the Spannenburg old material. The GIH-pellets produced from fresh Spannenburg residual and Ferrosorp Plus showed somewhat similar uptake at low equilibrium concentrations of As, however at higher equilibrium concentrations the GIH-pellets produced from Spannenburg residual seemed to perform better than the Ferrosorp Plus.

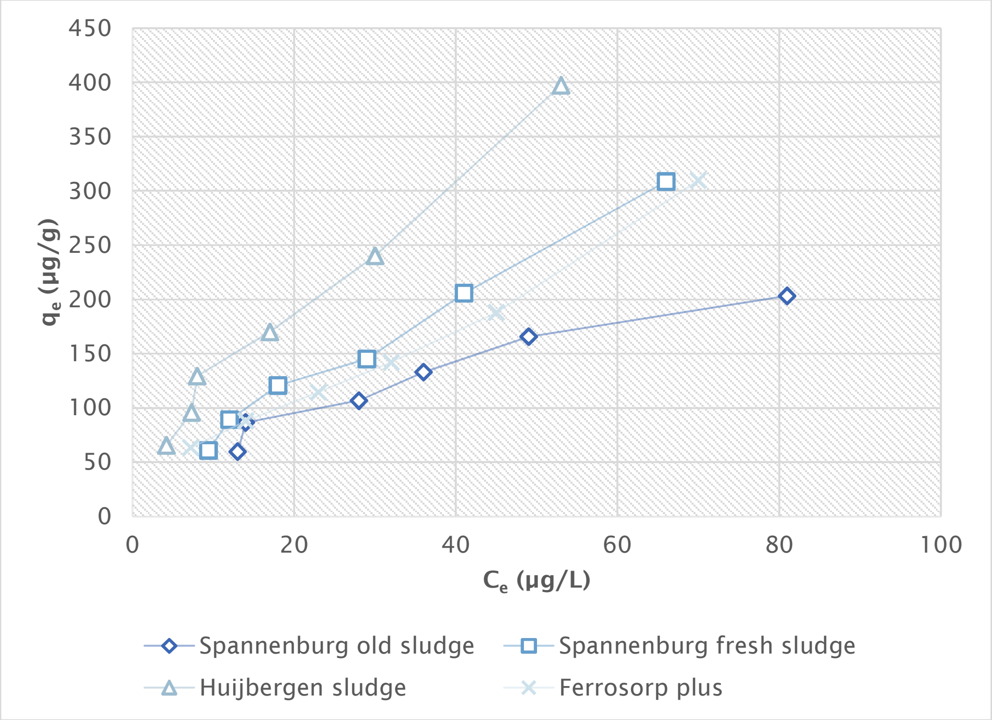


FIGURE 28 ADSORPTION ISOTHERMS OF As ONTO GIH-PELLETS AND FERROSORP PLUS AT 15°C.

FREUNDLICH AND LANGMUIR MODELS WERE APPLIED TO EVALUATE THE ADSORPTION ISOTHERM DATA. THESE MODELS HAVE BEEN DESCRIBED CHAPTER 5. Table 24 and Table 25 present the coefficients of determination (R^2) and the parameters of Freundlich and Langmuir models respectively. It can be seen that in general both models fit the adsorption data reasonably well. In order to determine which model would be best, more experimental data should be available.

In Table 24 K_F is the Freundlich constant related to the adsorption capacity and n is the dimensionless empirical parameter representing the energetic heterogeneity of the adsorption sites (Fierro, Torné-Fernández et al. 2008). Both K_F and n are measures of the adsorption capacity and intensity of adsorption (Malik 2004). At $1/n = 1$ linear adsorption takes place, if $1/n<1$ the adsorption process is chemical in nature, and if $1/n>1$ it is cooperative. The values of the K_F clearly show that the GIH-pellets produced from Huijbergen residual has the highest adsorption capacity. The K_F of Ferrosorp Plus and GIH-pellets produced from old Spannenburg residual are in the similar order of magnitude. The values obtained for $1/n$ are <1, indicating chemisorption was involved in the uptake of As by all the tested adsorbents. In case chemisorption is involved, pseudo-second order kinetic modelling can be applied, as is described in Appendix 9.

In Table 25 q_m is the maximum sorption capacity and K_L is the adsorption equilibrium constant. If $R_L>1$ adsorption is unfavorable, if $R_L = 1$ it is linear, if $0<R_L<1$ adsorption is favorable, and if $R_L=0$ irreversible adsorption will take place (Weber and Chakravorti 1974). It can be seen that the values obtained for R_L are between 0 and 1. This indicates that adsorption of As on all the tested adsorbents was favorable. Furthermore, q_m determined from the intercept of the linearized Langmuir isotherms show the following order of adsorbents based on their adsorption capacity: Spannenburg fresh sludge>Huijbergen>Spannenburg old sludge>Ferrosorp Plus. This order of adsorbents based on their adsorption capacity determined from Langmuir model is different from the q_e determined from pseudo-second order model in the kinetic modeling. This is also different from what was observed in case of orthophosphate. It is advised to perform the adsorption tests at higher As concentrations. A higher initial As concentration would provide the necessary driving force to overcome the resistance to the mass transfer of As between the aqueous phase and the solid phase. The increase in initial As concentration would also enhance the interaction between As and the adsorbents. The combined effect may result in higher uptake of As at equilibrium.

TABLE 24 FREUNDLICH ADSORPTION PARAMETERS FOR As ADSORPTION.

Adsorbents	**R^2**	**K_F (µg/g)(µg/L)^n**	**1/n**
Spannenburg old sludge	0.938	14.8	0.606
Spanneburg fresh sludge	0.978	11.9	0.760
Huibergen sludge	0.975	26.7	0.669
Ferrosorp Plus	0.966	15.1	0.674

TABLE 25 LANGMUIR ADSORPTION PARAMETERS FOR As ADSORPOTION.

Adsorbents	**R^2**	**q_m (µg/g)**	**K_L (L/µg)**	**R_L**
Spannenburg old sludge	0.885	312.5	2.1×10^{-2}	0.316
Spanneburg fresh sludge	0.969	667	1.1×10^{-2}	0.463
Huibergen sludge	0.973	500	3.6×10^{-2}	0.215
Ferrosorp Plus	0.938	285.7	3.7×10^{-2}	0.209

7.4 Adsorption experiments with pellets made with cement and water glass

Preliminary batch experiments to determine the adsorption of As were performed using the pellets made by means of the rotating disk process, using cement of water glass as binder material. The results showed that in 48 hours 70% of the initial As concentration in the solution (100 µg/L) was adsorbed by both types of pellets. The percentage of As uptake was not affected by the choice of binder, i.e. uptake of As was of similar order of magnitude for the GIH-pellets containing either the cement or water glass. Moreover, the As uptake with 1% and 5% binder was similar (70%) for both type of materials.

7.5 Conclusions and recommendations

From the content presented in this chapter the following conclusions can be drawn:

Regarding kinetics, GIH-pellets and Ferrosorp showed similar adsorption trends for As.

Regarding adsorption equilibrium, it is clear that the GIH-pellets have a remarkably high adsorption capacity for As (according to Table 25 significantly higher than the adsorption capacity of Ferrosorp Plus). However, this could not yet be correlated to either the iron content or the specific surface area, as the initial As concentration in the experiments probably was too low. It is recommended to perform adsorption isotherms with higher initial As concentrations and at a longer equilibration time.

8 Arsenic adsorption at pilot scale

8.1 Introduction

Pilot scale experiments were carried out at two drinking water treatment facilities in the Netherlands, namely Katwijk (water company Dunea) and Prinsenbosch (water company Brabant Water). The pilot experiments were aimed at evaluating the behavior of GIH-pellets as As adsorbents in varying field conditions and comparison of the adsorption performance with Ferrosorp Plus. The performance of GIH-pellets in removing arsenic (As) to <1 µg/L was evaluated. Since As concentrations were low in the streams that had to be treated at Katwijk and Prinsenbosch, and the lab scale experiments had shown high adsorption capacity for GIH-pellets, it was expected that the pilot experiments would take a long time to reach breakthrough of the filters. It was decided to use the GIH-pellets that were produced at Agravis by extrusion pelletization, using residual of Spannenburg. These were the same pellets that had been used in the pilot scale experiments for phosphate removal at Amsterdam, however, for the sake of making a reasonable comparison with Ferrosorp Plus the pellets were crushed and sieved to obtain a similar particle size as Ferrosorp Plus.

The pilot installations were mainly operated by the process technologists at the drinking water facilities. KWR provided assistance during the start-up and shut-down of the installations.

8.2 Materials and methods

8.2.1 Pilot experiments at Katwijk

8.2.1.1 Influent

Drinking water treatment facility Katwijk is a surface water treatment facility, using surface water from the Afgedamde Maas, that has been pretreated in Bergambacht (coagulation, sedimentation, micro sieves and sand filtration), and then is filtrated by the dunes. The dune effluent is treated in a series of steps, including powdered activated carbon dosing, cascade aeration, pellet softening with caustic soda, rapid sand filtration and finally slow sand filtration. After the treatment, the As concentration in the produced drinking water is averaged at 3.0 µg/L. For the pilot experiments, the effluent of the rapid sand filters was used as feed. The choice was based on two reasons, firstly, the presence of low concentrations of suspended solids, secondly the presence of As(V) as the dominant form of As. It has been previously shown that As(V) adsorbs more efficiently to amorphous iron(hydr)oxides compared to As(III) (Pierce and Moore 1982). Table 26 presents the average quality of the pilot influent.

TABLE 26 AVERAGE WATER QUALITY OF THE PILOT INFLUENT AT KATWIJK.

Parameter	Unit	Concentration
Dissolved oxygen	mg O_2/L	9.9±0.38 (n=8)
pH	-	8.48±0.09 (n=104)
Turbidity	FTE	0.01±0.02 (n=106)
Hardness	mmol/L	1.44±0.06 (n=53)
Alkalinity	mg HCO_3/L	174.7±5.20 (n=53)
Arsenic	µg As/L	3.0±0.4 (n=26)
Ammonia	mg NH_4/L	0.006±0.001 (n=53)
Calcium	mg Ca/L	43.9±4.68 (n=105)
Magnesium	mg Mg/L	8.2
Sodium	mg Na/L	52.2±3.7 (n=9)
Iron	mg Fe/L	0.003
Manganese	mg Mn/L	0.001
Dissolved organic carbon	mg C/L	2.4±0.15 (n=27)
Orthophosphate	mg PO_4/L	0.15±0.02 (n=8)
Total phosphate	mg PO_4/L	0.17±0.02 (n=8)

8.2.1.2 Pilot setup and experimental settings

The pilot setup consisted of 5 columns, mounted on a movable skid (Figure 29). The diameter of each column was 5 cm and the height was 100 cm. The columns could be fed either from top or from bottom, however in this study the columns were fed only from the top (down-flow mode).

In the pilot experiments two types of sorbents were used; GIH-pellets (particle size 0.5-2.0 mm) and Ferrosorp Plus (particle size 0.5-2.0 mm). The GIH-pellets were produced by extrusion of the Spannenburg residual at Agravis (see section 3.3 and chapter 6). Before transport to Katwijk the material had been grounded and subsequently sieved in the required size range at Boekel Chemical Repackaging B.V. The Ferrosorp Plus was supplied by HeGo Biotech GmbH (Germany).

In the columns with GIH-pellets empty bed contact times (EBCTs) of 3 min, 5 min and 10 min were tested and for Ferrosorp Plus EBCTs of 3 min and 5 min were tested. Table 27 presents the overview of column dimensions and experimental settings.

FIGURE 29 PILOT SETUP USED FOR ADSORPOTION EXPERIMENTS AT KATWIJK

TABLE 27 DIMENSIONS OF THE PILOT COLUMNS AND EXPERIMENTAL SETTINGS TESTED AT KATWIJK.

Column #	Adsorbent	Column diameter	Column height	Adsorption bed height	Bed volume	Influent flow	Empty bed contact time
1	GIH-pellets	5 cm	100 cm	55 cm	1.1 L	21.6 L h^{-1}	3 min
2	GIH-pellets	5 cm	100 cm	91.5 cm	1.8 L	21.6 L h^{-1}	5 min
3	GIH-pellets	5 cm	100 cm	91.5 cm	1.8 L	10.8 L h^{-1}	10 min
4	Ferrosorp	5 cm	100 cm	55 cm	1.1 L	21.6 L h^{-1}	3 min
5	Ferrosorp	5 cm	100 cm	91.5 cm	1.8 L	21.6 L h^{-1}	5 min

8.2.1.3 Pilot operation, sampling and analysis

The pilot experiments started on June 27th 2016 and were stopped on February 3rd 2017. The GIH-pellets and Ferrosorp Plus were washed with the treatment plant effluent of Katwijk to remove fine particles resulting from transport and handling of the adsorbents. After washing, the columns were filled with the adsorbents up to the required bed heights (Table 27). The columns were tapped with a rubber hammer during filling in order to avoid air entrapment in the adsorption beds. After the columns had been filled, they were sealed from the top and flow of the influent was started.

The first samples were taken from each of the columns after 4 days of continuous operation. Meanwhile the flows were monitored regularly and adjusted to comply with the initial settings. The first sampling (on the July 1st 2016) included collection of filtered (through 0.45 µm) and unfiltered samples for the analysis of arsenic, iron, manganese, total organic carbon and phosphate. In the unfiltered samples the total concentrations of these elements were measured, while in the filtered samples the dissolved concentrations were determined. After this first sampling the regular sampling program started which included collection of unfiltered samples only.

As part of the regular sampling program, the operators at Katwijk checked the influent and effluent flows, bed height of each column and effluent pH, and collected samples 2-3 times per week in designated bottles. However, only the samples of the last sampling event of the week (usually of Friday) were sent to the laboratory for analysis. This means samples from only one sampling event per week were analyzed. The samples from the other sampling events of the given week were stored in the refrigerator until the laboratory had reported the results. If the results did not show anomalies, these samples were discarded.

All the samples were analyzed at HWL Laboratory.

8.2.2 Pilot experiments at Prinsenbosch

8.2.2.1 Influent

The drinking water treatment plant of Prinsenbosch is a conventional groundwater treatment plant (aimed at iron, manganese, and ammonia removal). The treatment process includes cascade aeration followed by rapid sand filtration. The effluent of the rapid sand filters contains 2.3 µg/L As, on average. As(V) is the dominant form of As in the effluent of rapid sand filters. For the pilot experiments, the effluent of the rapid sand filters was used as feed. Table 28 provides an overview of the average influent water quality of the pilot setup.

TABLE 28 AVERAGE WATER QUALITY OF THE PILOT INFLUENT AT PRINSENBOSCH.

Parameter	**Unit**	**Measurement**
pH	-	7.7
Dissolved oxygen	mg O_2/L	9.1
Hardness	mmol/L	1.74
bicarbonate	mg HCO_3/L	218
Carbon dioxide	mg/L	6.5
Turbidity	FTE	<0.12
Magnesium	mg Mg/L	5.1
Turbidity	mS/m	32.5
Arsenic	µg As/L	2.7
Iron	mg Fe/L	<0.01
Manganese	mg Mn/L	<0.01
Calcium	mg ca/L	61
Ammonia	mg NH_4/L	<0.03
Total organic carbon	mg C/L	1.72
Orthophosphate	mg PO_4/L	0.06
Silica	mg SiO_2/L	18.5
Sulphate	mg SO_4/L	<1

8.2.2.2 Pilot setup and experimental settings

The pilot setup consisted of 2 columns (Figure 30). The diameter of each column was 15 cm and the height was 150 cm. The columns could be fed either from top or from bottom, however in this study the columns were fed only from the top (down-flow mode).

Unlike Katwijk, where also Ferrosorp Plus was applied as an adsorbent, at Prinsenbosch only the GIH-pellets (particle size 0.5-2.0 mm) were used for pilot scale experiments. Two settings of the EBCT were applied in the experiments: an EBCT of 3 min and 5 min. Table 29 presents the overview of column dimensions and experimental settings used at Prinsenbosch.

8.2.2.3 Pilot operation, sampling and analysis

The pilot experiments were started on September 29th 2016 and were continued until March 2017. In this report data till February 17th 2017 have been used. The GIH-pellets were washed and the columns were filled following the same procedure that was followed at Katwijk. After the columns had been filled with adsorption media, they were sealed from the top and the flow was initiated.

The first samples were taken from each of the columns after one day of operation. The first sampling (on the Sep 30th 2016) included collection of filtered (through 0.45 μm) and unfiltered samples for the analysis of arsenic, iron, manganese, total organic carbon, phosphate. The concentration in the unfiltered samples was used to determine the total concentration of these elements and the filtered samples were used to measure their dissolved concentrations. After the first sampling the regular sampling program started which included collection of unfiltered samples only.

The regular sampling and monitoring program was similar to the one implemented at Katwijk. All the samples were analyzed at Aqualab Zuid.

FIGURE 30 PILOT COLUMNS FILLED WITH GIH-PELLETS AT PRINSENBOSCH.

TABLE 29 DIMENSIONS OF THE PILOT COLUMNS AND EXPERIMENTAL SETTINGS TESTED AT PRINSENBOSCH.

Column #	Column diameter	Column height	Adsorption bed height	Bed volume	Influent flow	Empty bed contact time (EBCT)
1	15 cm	150 cm	100 cm	17.6 L	352 L h^{-1}	3 min
2	15 cm	150 cm	100 cm	17.6 L	211 L h^{-1}	5 min

8.3 Results and Discussion

8.3.1 Pilot experiments at Katwijk

The pilot installation consisted of five columns. Three of the them had been filled with the GIH-pellets and the other two had been filled with Ferrosorp Plus. In columns with GIH-pellets, EBCTs of 3 min, 5 min and 10 min were applied and in the columns with Ferrosorp Plus an EBCT of 3 min and 5 min was applied. Figure 31 presents the As adsorption curves. The adsorption curves are obtained by plotting the ratio of the aqueous concentration of As and the initial concentration (c/c_0) versus the number of treated bed volumes. It can be seen that the data are rather scattered (Figure 31). The data scatter is mainly attributed to variability in influent water quality and variability of flow through the columns from time to time. Another source of variability might be analytical uncertainty associated with measurements of very low As concentrations (<0.5 µg/L).

Figure 31 shows that the shape of the adsorption curves is comparable for GIH-pellets and Ferrosorp Plus. In a packed-bed adsorptive media system, a mass transfer zone (MTZ), where active adsorption of solute occurs, is established initially at the inlet of the bed and gradually migrates deeper into the bed. Solute eventually breaks through the bed with increasing concentrations in the system effluent. From the shape of the adsorption curves shown in Figure 31 it seems that the length of the MTZ was large in case of both the adsorbents. It should be noted that in general the lower the slope of the curve, the longer the MTZ. It can be seen that the removal of As improved with increase in EBCT for both the adsorbents, however the influence of EBCT seems to be more pronounced in the case of GIH-pellets.

Nearly maximum adsorption capacity is reached when C/C_o reaches 0.9. In some cases, when adsorption beds are not fully exhausted, the use of inflection point (mid-point) in the breakthrough curve becomes helpful, especially for comparing the performance of different adsorbents. Table 30 provides an overview of the number of bed volumes treated with respect to the three C/C_o cut-offs. It should be noted that for Katwijk the treatment objective was achieving <1 µg/L As in the effluent. This corresponds to C/C_o=0.3, based on reducing on average 3 µg As/L to <1 µg As/L. It can be seen in Figure 31 that the adsorption beds were not exhausted for EBCT of 5 min and 10 min, for both types of adsorbents. Only the Ferrosorp Plus based adsorption column, with an EBCT of 3 min, was exhausted after treating 93 000 bed volumes. Since the GIH-pellets based column with an EBCT of 3 min had not yet been exhausted at 93 000 bed volumes, it can be concluded that the adsorption capacity of GIH-pellets appears to be higher.

At Katwijk the treatment objective was to achieve <1 µg/L As, corresponding to C/C_o=0.3. It can be seen in Figure 31 and Table 30 that at an EBCT of 3 min the adsorption column with GIH-pellets produced 9000 bed volumes and Ferrosorp Plus produced 8000 bed volumes until the treatment objective of C/C_o of 0.3 was compromised. At the EBCT of 5 min the difference of As adsorption performance is more pronounced, as can be observed in Table 30, as the number of bed volumes produced by GIH-pellets was significantly higher compared to the number of bed volumes produced by Ferrosorp Plus. It can be concluded that the As adsorption performance of both the GIH-pellets and Ferrosorp Plus increased with increasing EBCT, however the performance of GIH-was a little better than that of the Ferrosorp Plus. The GIH-pellets based column with an EBCT of 10 min did not show As breakthrough above C/C_o even after 30 000 bed volumes had been treated. Again this confirms that the adsorption performance improves with increasing EBCT. Appendix XI presents the effluent water quality of the columns with GIH-pellets.

A comparison at C/C_o=0.5 can also be made. Table 30 shows that the GIH-pellets based columns treated 27 000 and 50 000 bed volumes at an EBCT of 3 min. and 5 min. respectively, and the Ferrosorp Plus based columns treated 24000 and 46000 bed volumes at an EBCT of 3 min. and 5 min. respectively. It is evident that the number of bed volumes treated was about 10% higher in case of GIH-pellets.

Based on the adsorption data the total capacity of two Ferrosorp Plus pilot columns has been calculated (Table 30), defining breakthrough at C/C_0=0.9. However, the adsorption capacity of the other columns (GIH-pellets EBCT=3 min, 5 min, 10 min) has not been calculated because the columns had not been exhausted and approximation then could be misleading. Nevertheless, it can be concluded that the total column capacity would be higher than the Ferrosorp adsorption capacity, because at an EBCT of 3 min the Ferrosorp bed had been exhausted.

FIGURE 31 ARSENIC BREAKTHROUGH CURVE OF GIH-PELLETS (TOP) AND FERROSORP PLUS (BOTTOM) AT KATWIJK.

TABLE 30 PERFORMANCE CHARACTERISTICS OF PILOT COLUMNS AT KATWIJK.

	GIH-pellets		**Ferrosorp Plus**			
	Bed volumes at $C/C_o=0.3$	**Bed volumes treated at $C/C_o=0.5$**	**Bed volumes treated at $C/C_o=0.3$**	**Bed volumes treated at $C/C_o=0.5$**	**Bed volumes treated at $C/C_o=0.9$**	**Total column capacity (µg g^{-1} media)**
EBCT=3 min	9000	27000	8000	24000	93000	125.9
EBCT=5 min	25000	50000	20000	46000	Not reached	241.4

The pilot columns were monitored for constituents other than As also, including pH, iron, orthophosphate and DOC. The orthophosphate results are of particular interest because it is often reported that orthophosphate competes with As for the adsorption sites on iron(hydr)oxides. Figure 32 presents the orthophosphate breakthrough curves for columns with GIH-pellets and Ferrosorp Plus operated at an EBCT of 3 min and 5 min. It can be seen that substantial adsorption of orthophosphate took place, which in all cases decreased in time. It means that the adsorption of both As and orthophosphate was taking place in the columns. For GIH-pellets adsorption of orthophosphate was noticeably lower compared to Ferrosorp Plus. It might be due to higher phosphate content in the residual of Spannenburg compared to Ferrosorp Plus. The influence of the phosphate content of the residuals on phosphate adsorption from water should be further studied. An interesting thing to note is that the concentration of orthophosphate in the influent of pilot columns was averaged at 158.6 µg/L, much higher than the average As concentration in the influent (3 µg/L). Competitive removal of As and orthophosphate by GIH-pellets should be studied in detail.

Figure 33 shows the DOC breakthrough curves for columns with GIH-pellets and Ferrosorp Plus operated at an EBCT of 3 min and 5 min. It can be seen that in the beginning of the pilot experiments some DOC was mobilised from both adsorption media. The DOC concentration in the influent of pilot columns was averaged at 2.41 mg/L. Approximately 0.5 mg DOC/L was mobilised from the GIH-pellets and maximum 0.12 mg/L of DOC was mobilised from Ferrosorp Plus. It should be noted that the GIH-pellets were based on the residual from drinking water facility Spannenburg. This material contained 6.5% of organic compounds (Table 4). The information on the organic content of the Ferrosorp Plus is not available. It can be seen in Figure 33 that the mobilisation of DOC decreased with time for both adsorbents, however it seems that the Ferrosorp Plus “levelled-off” earlier compared to GIH-pellets. More frequent sampling during the first few weeks of pilot start-up (first 10 000 bed volumes) could highlight the trend better. Nevertheless, it is evident that the first 10 000 bed volumes are critical in relation to DOC mobilisation.

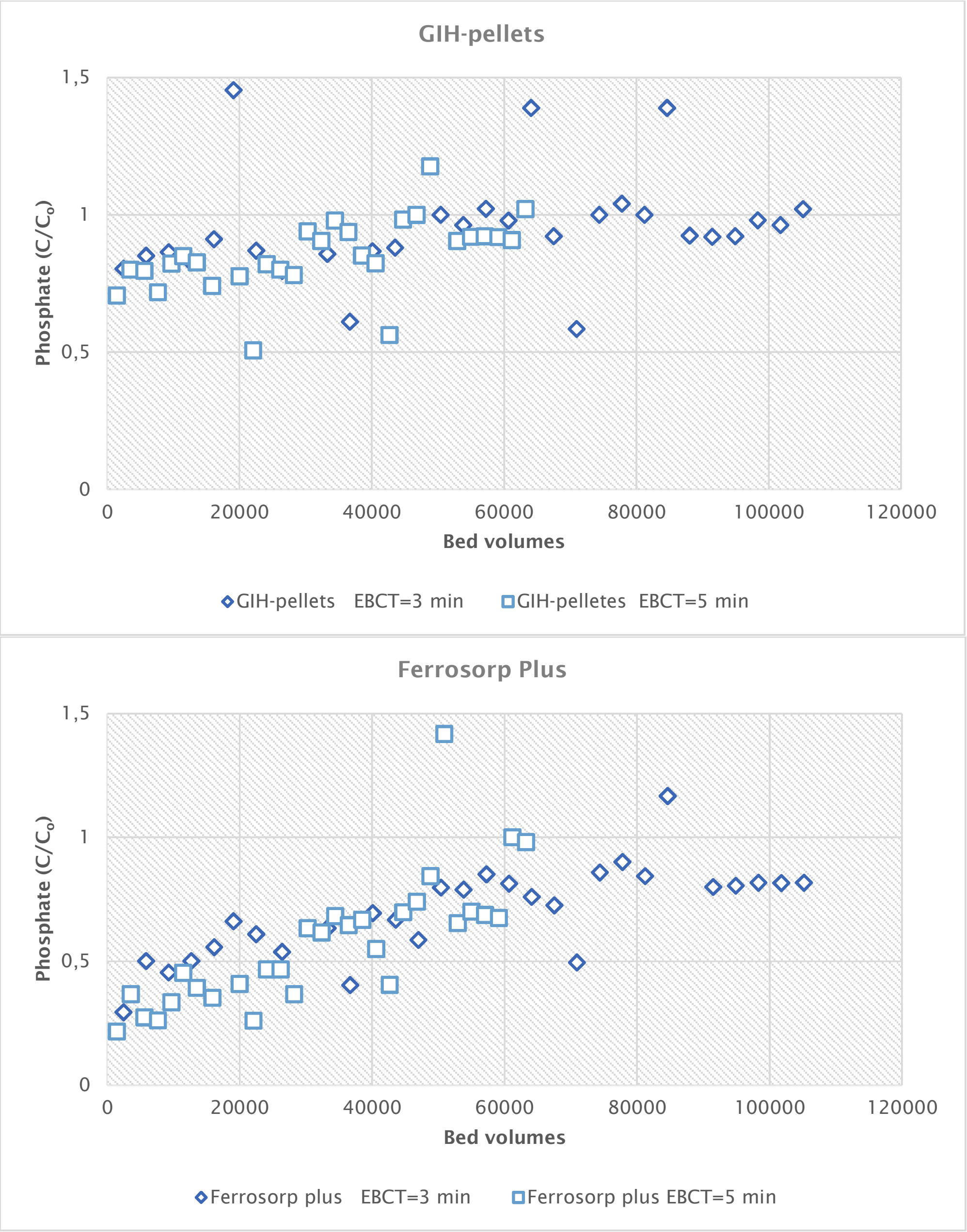


FIGURE 32 ORTHOPHOSPHATE BREAKTHROUGH CURVE OF GIH-PELLETS (TOP) AND FERROSORP PLUS (BOTTOM) AT KATWIJK.

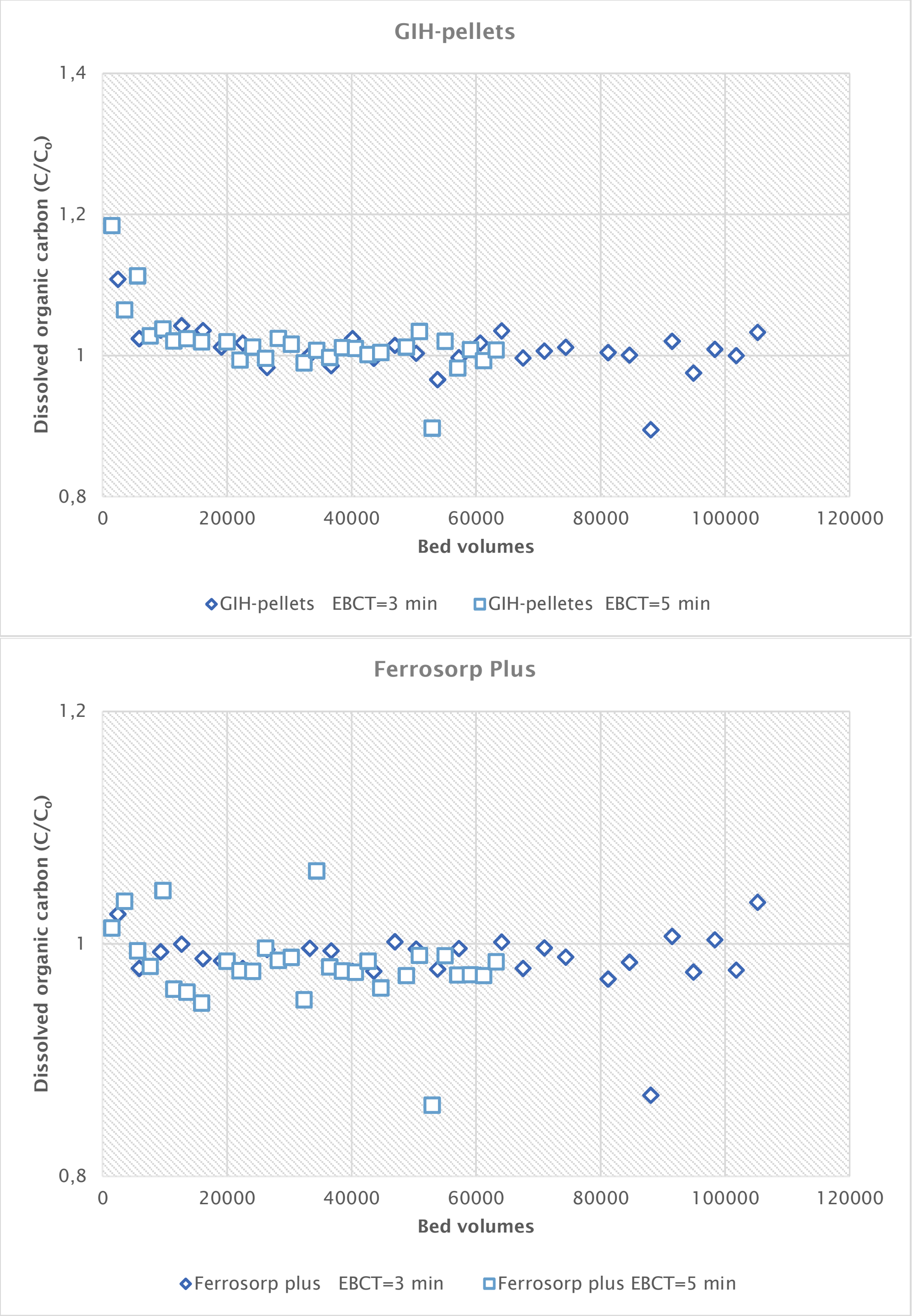


FIGURE 33 TOTAL ORGANIC CARBON BREAKTHROUGH CURVE OF GIH-PELLETS (TOP) AND FERROSORP PLUS (BOTTOM) AT KATWIJK.

8.3.2 Pilot experiments at Prinsenbosch

In the pilot experiments at Prinsenbosch the setup included two columns. Both columns contained GIH-pellets, however in one of the columns an EBCT of 3 min was tested and in the other column an EBCT of 5 min. Figure 34 presents the As breakthrough curves for the pilot columns. The breakthrough curves are obtained by plotting the arsenic concentration as C/C_0 versus number of treated bed volumes. It can be seen in Figure 34 that the columns had not been exhausted (C/C_o=0.9) in the given time period, even after treating more than 65 000 bed volumes at an EBCT of 3 min, representing high As adsorption performance of the GIH-pellets. The shape of both the breakthrough curves is comparable, however a higher removal at an EBCT of 5 min is evident. Like Katwijk, from the shape of the breakthrough curves it seems that the length of the MTZ was large.

The most critical parts of the breakthrough curve are actual breakthrough of the arsenic in relation to the desired effluent concentration (in this case C/C_o=0.4, based on reducing 2.3 µg As/L to <1 µg As/L). Another important factor is exhaustion of the material at nearly ultimate adsorption capacity (C/C_o=0.9). The latter is generally used to calculate the total adsorption capacity of the adsorption bed. However, as Figure 34 shows, the adsorption beds had not been exhausted. Even the breakthrough curve with an EBCT of 5 min did not reach the inflection point (C/C_o=0.5). This has induced a complication in calculating the adsorption capacity of the GIH-pellets in the field conditions of Prinsenbosch. At least a complete breakthrough curve at an EBCT of 3 min would be required for reliable calculation. However, this had not yet been reached.

At Prinsenbosch the treatment objective was to achieve <1 µg/L As, corresponding to C/C_o=0.4. It can be seen in Figure 34 and Table 31 that the adsorption column with an EBCT of 3 min produced 20 000 bed volumes and the column with an EBCT of 5 min produced 35 000 bed volumes until the C/C_o of 0.4 was reached. This means that the As adsorption performance increased with increasing EBCT. A similar increase in As adsorption was noticed at Katwijk also. However, the number of bed volumes that can be treated at Prinsenbosch until C/C_o cut-off of 0.4 is approximately 10 000 bed volumes higher compared to Katwijk. This probably is because the influent As concentration at Prinsenbosch is lower (2.3 µg/L) compared to Katwijk (3 µg/L).

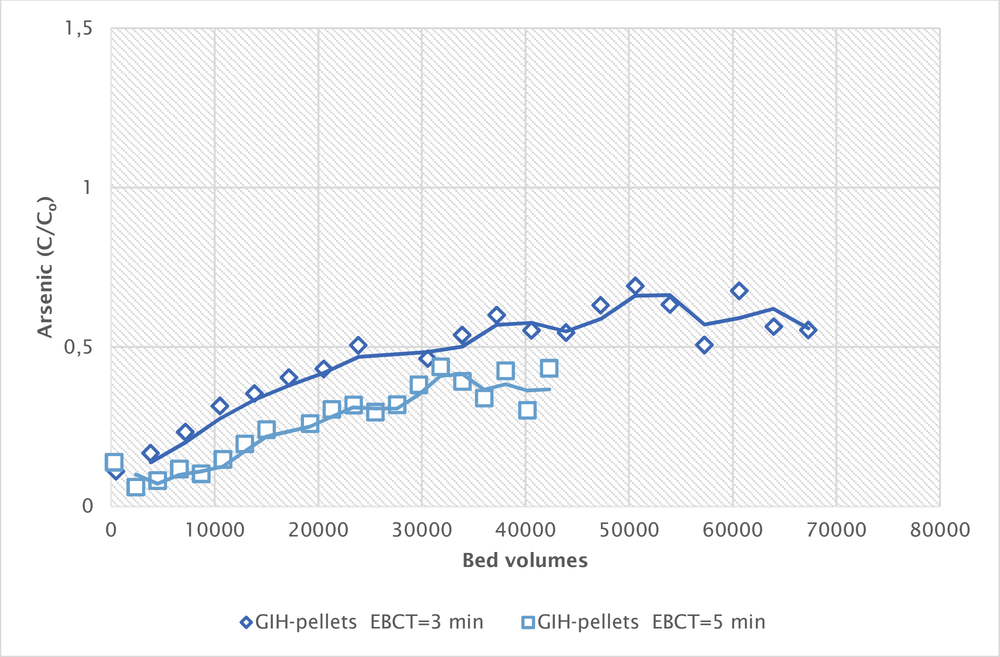


FIGURE 34 ARSENIC BREAKTHROUGH CURVE OF GIH-PELLETS AT PRINSENBOSCH.

TABLE 31 PERFORMANCE CHARACTERISTICS OF PILOT COLUMNS AT PRINSENBOSCH.

	GIH-pellets	
	Bed volumes at C/C_o=0.4	**Bed volumes treated at C/C_o=0.5**
EBCT=3 min	20000	32000
EBCT=5 min	35000	Not reached

Figure 35 presents the orthophosphate adsorption curves for the Prinsenbosch columns. It can be seen that some mobilisation of orthophosphate may have occurred from the GIH-pellets at the start. The curves seem to level off after 10 000 bed volumes. However, there are insufficient data to draw any real conclusions on this topic. Nevertheless, it is clear that orthophosphate removal was not significant in the GIH columns at the Prinsenbosch pilot. Contrasting to this, at Katwijk orthophosphate adsorption by GIH-pellets was significant. The pilot data show that the average concentration of orthophosphate in the column influent at Prinsenbosch was 63.9 µg/L. Although this concentration is 2.5 times lower than the concentration in Katwijk, it is still much higher than the As concentration in the influent of Prinsenbosch (averaged at 2.3 µg/L). A systematic evaluation of the influence of various parameters (e.g. pH, silicate, nitrate, bicarbonate etc.) on competitive As and orthophosphate adsorption is needed.

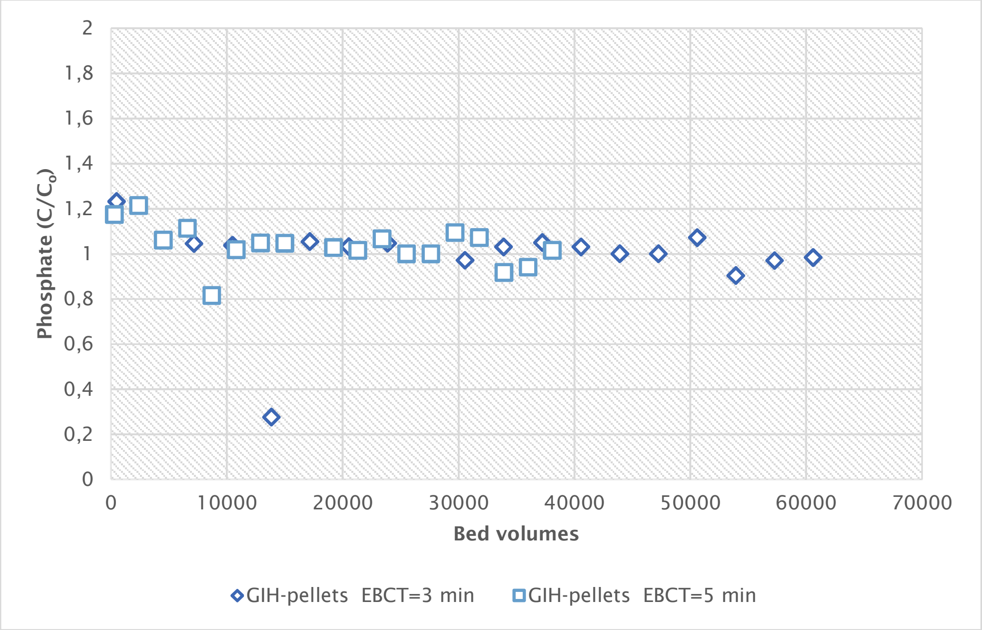


FIGURE 35 ORTHOPHOSPHATE BREAKTHROUGH CURVE OF GIH-PELLETS AT PRINSENBOSCH.

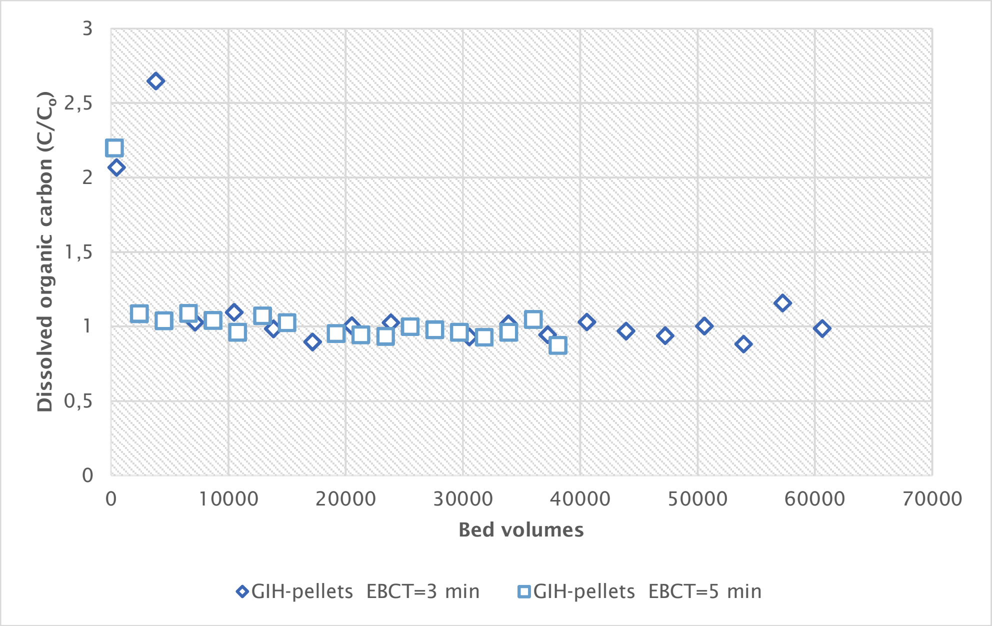


FIGURE 36 DISSOLVED ORGANIC CARBON BREAKTHROUGH CURVE OF GIH-PELLETS AT PRINSENBOSCH.

Figure 36 presents the DOC breakthrough curves for columns operated at an EBCT of 3 min and 5 min. It can be seen that in the beginning of the pilot experiments some DOC was mobilised from the adsorption media. The DOC concentration in the influent of pilot columns was averaged at 1.85 mg/L. The effluent DOC concentration approximately doubled, however decreased to match the influent DOC concentration after 2400 bed volumes at an EBCT of 5 min and after 4500 bed volumes at an EBCT of 3 min. This means that a higher EBCT decreased the number of bed volumes with elevated DOC concentrations. Since the frequency of sampling was once per week only, a clear trend of decrease in DOC mobilisation was not obtained in the first period of the pilot experiments. More frequent sampling during the first weeks of the pilot start-up (first 10 000 bed volumes) would have highlighted the trend better. Nevertheless, it is evident that the first 5 000 bed volumes are critical in relation of DOC mobilisation.

Figure 37 presents the manganese breakthrough curves for both the columns. Two interesting phenomena can be observed. Firstly, the mobilisation of manganese from the GIH-pellets in the beginning of the trials, and secondly, consistent removal of manganese in the later phase. It seems that in the column with an EBCT of 5 min the equilibrium was reached earlier (in terms of bed volumes). The manganese concentration in the column influent was averaged at 5.1 µg/L.

The absolute concentrations of As, phosphate and DOC in the influent and effluent of columns are provided as Appendix XI.

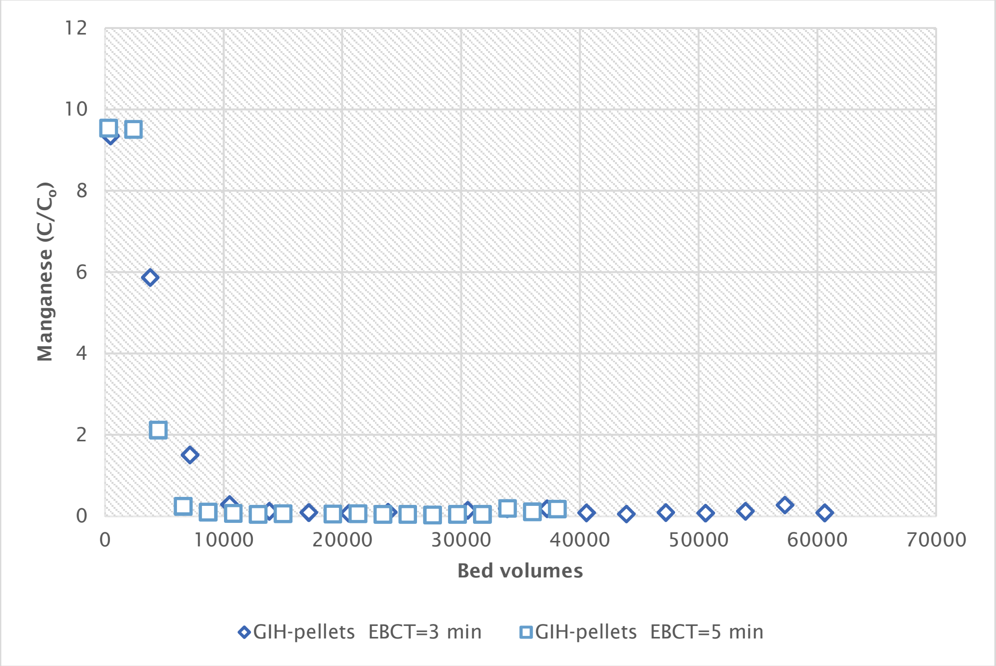


FIGURE 37 MANGANESE BREAKTHROUGH CURVE OF GIH-PELLETS AT PRINSENBOSCH.

8.4 Conclusions and recommendations

From the content presented in this chapter it can be concluded that:

Column tests with GIH-pellets are time consuming and thus expensive. Most adsorption columns at Katwijk and Prinsenbosch were not exhausted during the experimental period. This means that GIH-pellets exhibited a very high adsorption capacity for As, but the total bed adsorption capacity could not be calculated. Rapid Small Scale Column Tests (RSSCTs) can be an effective alternative in order to save time and money with such experiments.

The As adsorption capacity of GIH-pellets is high, slightly better or at least comparable to that of Ferrosorp Plus, which is a commercially established As adsorbent. The adsorption capacity increased with the increase in EBCT for both the materials. For example, adsorption capacity increased from 126 µg/g to 241 µg/g when the EBCT was increased from3 min to 5 min at Katwijk.

With an EBCT of 5 min, at Katwijk 25000 bed volumes can be treated with GIH based adsorbents in order to meet the <1 µg/L target and at Prinsenbosch 35000 bed volumes can be treated to meet the <1 µg/L target. This could be explained by a lower As concentration, lower orthophosphate concentration and lower pH at Prinsenbosch, however the influence of other water quality parameters e.g. silica, nitrate, sulphate, bicarbonate etc. should be studied.

Mobilisation of DOC and manganese from the GIH-pellets has been noticed in the beginning of the adsorption runs. The effluents contained manganese concentrations up to 90 µg/L in the beginning of the experiment. From a practical point of view water with such manganese concentrations is unsuitable for supply. However, different strategies can be adopted to cope with this. For example, recycling of the column effluent to upstream of rapid sand filter, or the use of a better quality drinking water treatment residual (with a lower manganese concentration) for the production of GIH-pellets. Based on the results of this study it is clear that mobilisation “levels-off” faster at a higher EBCT. Therefore, another strategy can be to rinse the GIH-pellets based beds with water at a higher EBCT (i.e. reduced filtration velocity).

The GIH-pellets in the pilot columns were disintegrated to some extent. This resulted in an unwanted pressure drop in the filter beds due to fines. The stability of the pellets needs to be further improved for smooth column operation and handling of the material during transport.

9 Conclusions and recommendations

9.1 Conclusions

9.1.1 Prior art study

A short patent search showed that the patens of e.g. Lanxess (c.q. Bayer) don't interfere with the processes described in this report.

9.1.2 Iron sludges and pelletization

Iron sludges from various drinking water facilities may differ largely, e.g. in the surface area available, the iron content, surface composition (and inhomogeneity), and crystallinity. Such factors may affect both the pelletization process as well as the pellet properties, including the adsorptive properties of the GIH-pellets. Furthermore, there are large differences in availability of different sludges. In order to obtain a more constant quality and permanent availability of the materials it was suggested to prepare a mixture consisting of sludges from eleven different production facilities.

The pelletization procedure applied at the laboratory was not suitable for up scaling. Two types of processes have been applied for this purpose by Agravis:

- Drying with waste heat, using an electric mole, followed by extrusion under high pressure
- Drum drying, followed by pelletization by means of a build-up pelletization process

The first process had some disadvantages, as dust generation during drying and loss of active surface by the high pressure applied. The second process doesn't show these disadvantages, giving good results regarding costs, adjustment of particles size, and probably adsorption capacity.

The pelletization process still has to be further optimized for transport and handling of the pellets, taking into account the ease of operation, dust formation, and up-scaling possibilities. Besides, it has to be determined how the pelletization process affects the adsorption capacity of the material. The high pressure applied in extrusion may e.g. decrease the pore volume and thus the adsorption capacity.

Whether and how CMC can be used as a binder depends on the GIH pellet production process. If CMC is used, it should be added to a wet sludge, in order to obtain good mixing. The presence of CMC doesn't affect the adsorptive properties nor the specific surface area available.

Two other binders also have been applied: cement and water glass. Although the first results on stability etc. seem to be favorable, more research into the applicability of these binders is required.

Several physical and chemical techniques can be applied to characterize iron sludges and GIH pellets. For commercial application of GIH pellets standards will have to be set. These standards should include iron content, specific surface area, and stability, and possibly also requirements on porosity will have to be determined. As to stability, although it has become clear that this is an important parameter, it still has to be decided how this parameter should be defined, and how it should be determined.

9.1.3 Adsorption of phosphate

Laboratory experiments showed that phosphate adsorption capacity depends on the type and origin of the iron sludge: highest adsorption capacity was obtained for Huijbergen sludge pellets, and lowest for Spannenburg “old” material. However, the adsorption capacity of GIH pellets is similar or even better as that of commercial iron(hydr)oxide adsorbents like Ferrosorp Plus.

Probably the adsorption capacity is related to the iron content of the material, although also the specific surface area may play a role. Besides, there are some indications that also polyacrylamide, used to facilitate dewatering, may have a negative impact. The adsorption isotherms of phosphate can be described by both the Langmuir and Freundlich model.

A pilot experiment at Waternet showed that surface water quality regarding phosphate concentration can significantly be improved by applying GIH pellets in a filter during a longer period of time (at least six months). For design purposes a maximum load of at least 4 g P/ kg dry matter can be assumed (about 20 g P/kg Fe), and a minimum residence time of 20 minutes.

9.1.4 Adsorption of arsenate

For the experiments with arsenate (As(V)) the initial concentration appeared not to have been high enough to obtain maximum adsorption, which made it more difficult to model the adsorption, and to determine the maximum adsorption capacity for arsenate. This appeared to be higher than had been expected.

Laboratory experiments showed that pellets from iron sludge show a good adsorption capacity for arsenate. It is not yet clear which parameter, like iron content or specific surface area, is most important for this adsorption.

After the extruded pellets (from the same batch that had been used in the phosphate pilot at Waternet) had been crushed, they have been applied in two pilot experiments on arsenate removal: one in Katwijk with Dunea, and one in Prinsenbosch at Brabant Water. It was found that during a period of about half a year high As-removal could be obtained, and no breakthrough was observed. Also, during several months the target arsenate concentration (< 1μg/L) could be reached. Thus, it was proven that GIH-pellets are suitable for arsenate removal. Unfortunately, it was not possible to carry out pilot experiments for a period longer than about half a year, as a result of which no breakthrough of arsenate could be observed, and no maximum adsorption capacity could be calculated. For design purposes an adsorption capacity of at least 240 mg As/ kg dry matter can be assumed at a residence time of 5 minutes.

A disadvantage of the use of GIH-pellets in drinking water production may be leakage of organic material and e.g. manganese to the water. This should be further investigated.

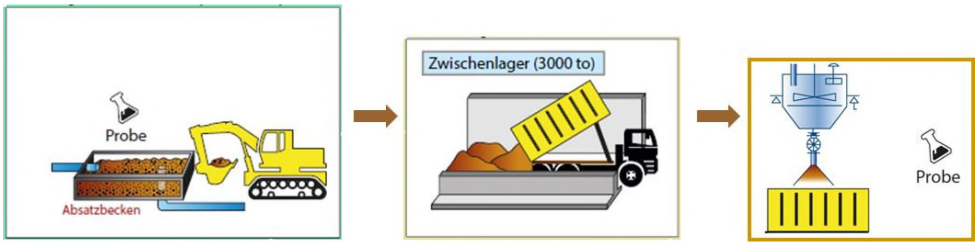
9.2 Recommendations

The first priority is to optimize the production process of GIH-pellets (choice of drying and pelletization method), the type of binder that is used, and the way it is applied.

Another priority is the choice of sludge or mixture of sludges to be used. This may also be of importance for the possible leakage of e.g. DOC, phosphate and metals (like manganese) from the GIH-pellets.

Leakage from the pellets., and e.g. the possibility of rinsing the pellets before application in order to avoid it, may also be an important research topic. Maybe certain sludge compositions should be preferred.

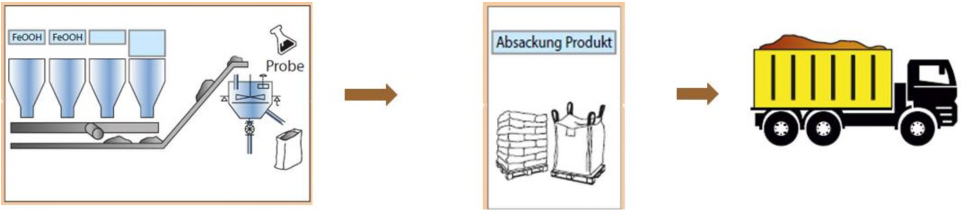
A possible production scheme, as proposed by Agravis, is shown in Figure 38.



Mining Fe-sludge
- OOWV (Oldenburgisch-Ostfriesische Wasserverband), etc
- Control of critical parameters

Storage in clamps
- Use of solar radiation for pre-drying

Drying
- min. 85% DS



Production
- Storage of dry FeO(OH)
- Sieving / Mixing
- Pelletizing
- Drying / Fractionating

Packaging
- Big Bag
- Sachet
- Bulk

Transport
- Storage plage
- Customer

FIGURE 38: PRODUCTION PROCESS FOR GIH PELLETS (INFORMATION FROM AGRAVIS)

It should be investigated whether phosphate loaded pellets can be used to bind hydrogen sulfide in biogas plants. The sulphur and phosphate containing pellets subsequently can be used as an additional nutrient source in the fermentation residue, which may be applied as an organic fertilizer in agriculture (Figure 39).

FIGURE 39: USE OF S AND P LOADED GIH PELLETS AS FERTILIZER IN AGRICULTURE

Adsorption experiments with arsenate should be repeated at higher arsenic concentrations, in order to be able to determine the maximum adsorption capacity of the material. How to deal with the As loaded pellets still will be a topic for further research.

10 Outlook

Iron residuals, originating from drinking water production, can be pelletized and applied for phosphate removal in surface water. Agravis has also done some experiments with iron pellets for the removal of H_2S from sulphide in biogas plants. It has become clear that phosphate loaded pellets subsequently may be used to remove H_2S from biogas. Afterwards, the pellets, loaded with phosphorous and sulphur may be applied as fertilizers, thus closing the loop (Figure 40).

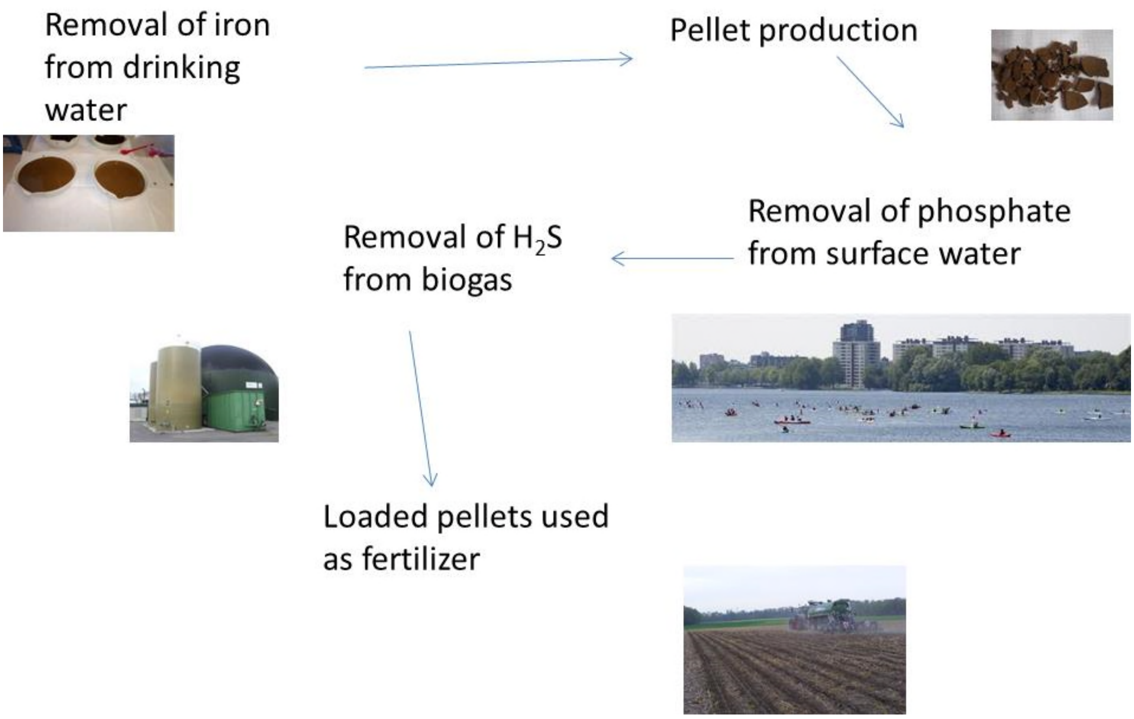


FIGURE 40: CLOSING THE LOOP WITH IRON PELLETS

Although GIH pellets appeared to show a good adsorption capacity for arsenate, at the moment there still is no good application for As loaded pellets. Therefore, after use in drinking water production plants these pellets would have to be treated as chemical waste material.

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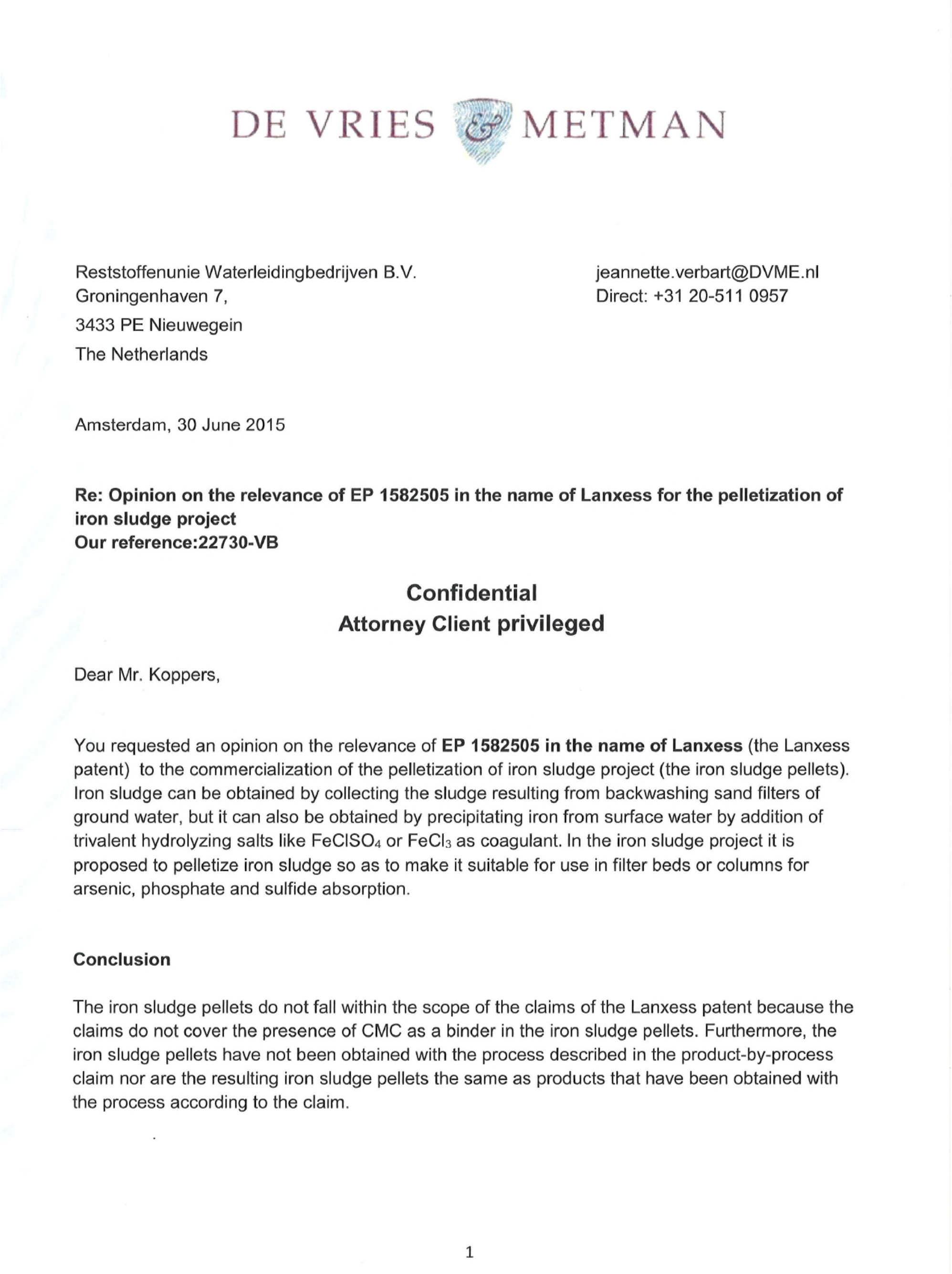
Appendix I Prior art study in the Netherlands

Evaluation by De Vries & Metman



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Amsterdam, 30 June 2015

Re: Opinion on the relevance of EP 1582505 in the name of Lanxess for the pelletization of iron sludge project
Our reference:22730-VB

Confidential
Attorney Client privileged

Dear Mr. Koppers,

You requested an opinion on the relevance of **EP 1582505 in the name of Lanxess** (the Lanxess patent) to the commercialization of the pelletization of iron sludge project (the iron sludge pellets). Iron sludge can be obtained by collecting the sludge resulting from backwashing sand filters of ground water, but it can also be obtained by precipitating iron from surface water by addition of trivalent hydrolyzing salts like $FeClSO_4$ or $FeCl_3$ as coagulant. In the iron sludge project it is proposed to pelletize iron sludge so as to make it suitable for use in filter beds or columns for arsenic, phosphate and sulfide absorption.

Conclusion

The iron sludge pellets do not fall within the scope of the claims of the Lanxess patent because the claims do not cover the presence of CMC as a binder in the iron sludge pellets. Furthermore, the iron sludge pellets have not been obtained with the process described in the product-by-process claim nor are the resulting iron sludge pellets the same as products that have been obtained with the process according to the claim.

Detailed Explanation

The iron sludge pellets

The iron sludge pellets are prepared by concentrating by means of drying iron(hydr)oxide sludge directly obtained from drinking water utilities. In the meantime an aqueous solution of a binder, carboxymethyl cellulose (CMC), is added and mixed with the sludge. The mixture is dried further at a temperature of about 105 °C. The dry material is grinded until a suitable particle size has been achieved, and then sieved. It has been found that the binder material gives the particles enough strength in order to resist shear stress without affecting adsorption capacity.
Chemical analysis indicates also the presence of other elements, like calcium, silicium, manganese and several trace constituents. The iron content ranges from about 30 to 50% on a dry weight basis. Calcium and silicium occur in concentrations of about 5%, all other elements are present in significantly lower concentrations. The specific BET surface area of the amorphous material is about 230 m^2/g, whereas the more crystalline material has a significantly lower BET surface area of only 120 m^2/g. In order to obtain adsorbents of a constant quality and high performance aqueous sludges of several utilities have to be combined resulting in a specified iron content or specific surface area.

The Lanxess patent

The lanxness patent exists in Germany, United Kingdom, France, Belgium, Spain, Hungary, Italy . As far as can be retrieved from the registers of the various national patent offices, the annuity fees have been paid and the necessary formalities for registering the patent in these countries have been fulfilled.

the claims

The lanxess patent claims :

1. *Granules consisting essentially of iron oxide and/or iron oxyhydroxide which have a turbidity by the turbidity test*
   specified in the description of < 300 FNU, obtainable by the mixture of essentially two components essentially
   consisting of
   1. a base and
   2. an Fe(III) solution
   wherein, if use is made of an FeCIS04 solution, it is added to the charged base.

Further the patent has claims directed to the use of these granules for removal of pollutants such as arsenic and phosphates from e.g. waste water.

In the description it is stated that granules having a turbidity according to the claim have an improved attrition resistance compared to commercially available iron oxide-containing granules. Said attrition resistance is stated to be connected to the turbidity of supernatant fluid when the particles are placed in suspension and mechanically agitated.

Claim interpretation:
Consisting essentially of language:
The claim recites that the granules consist essentially of iron oxide and/or ironoxyhydroxide. It further recites that it is obtainable by the mixture of essentially two components essentially consisting of a base, and an Fe(III) solution. It is accepted caselaw that the term consisting essentially of should be interpreted in that it allows the presence of other components in a claimed composition in addition to the components mandatory in the claim, provided that the essential characteristics of the claimed composition are not materially affected by their presence.
When looking at the description, it is clear that the whole patent is directed to granules that have an improved attrition resistance. The granules are stated to have sufficient mechanical stability even without the presence of organic binders or inorganic foreign binders. Said improved attrition resistance is obtained by the specific reaction between the base and the Fe(III) solution.

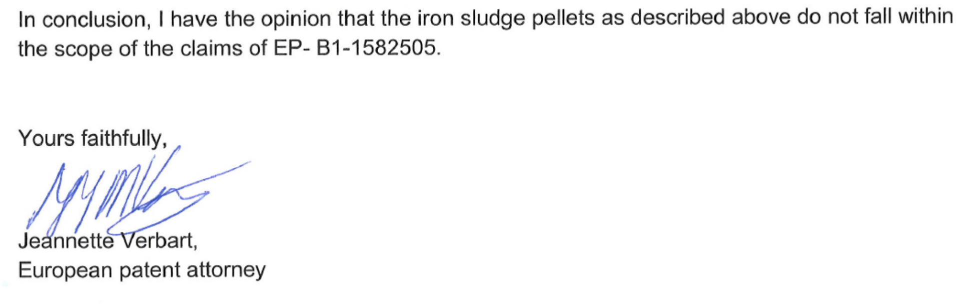
As explained above, the iron sludge pellets contain the binder CMC. It is also indicated by the researchers that is essential to add the CMC during drying in order to obtain pellets with sufficient attrition resistance. Without the CMC present, the pellets will fall apart. Thus, the presence of a binder such as CMC to iron oxide and/or iron oxyhydroxide will materially affect the characteristics of the granules. Therefore, CMC binder is not an allowable additional component in the composition of claim 1.
Therefore, pellets containing both iron oxide and/or iron oxyhydroxide and the binder CMC cannot be considered to fall within the scope of claim 1 of the Lanxess patent. Since the iron sludge pellets are outside the scope of claim 1, also the use claims can be considered irrelevant for the commercialization of the iron sludge pellets.

Obtainable by the mixture of two components essentially consisting of a base and an Fe(III) solution

The claim of the lanxess patent is a product-by-process claim. This means that products that are prepared by the process described fall within the scope of the claims, but also products that may have been prepared in a different way but have the same characteristics as a product prepared by the process claimed are within the scope of the claim. The iron sludge used to form pellets may be obtained by collecting the sludge resulting from backwashing sand filters of ground water. In this case, the iron oxide and/or iron oxyhydroxide has not been prepared by the mixture of a base and a trivalent iron solution. Question now is whether the iron sludge pellets which have been prepared with a different process, have the same characteristics as a product prepared by the process according to the claim. Since the pellets fall apart if no binder is present, the product obtained by drying iron sludge must be different from the products obtained when using the process of the lanxess patent.

The iron sludge may also be prepared by precipitating iron from surface water by addition of trivalent hydrolyzing salts like $FeClSO_4$ or $FeCl_3$ as coagulant. In this process also no base is mixed with an Fe(III) solution. Further, the product obtained with this process is also different from the product obtained with the process claimed.

These are additional arguments why the iron sludge pellets do not fall within the scope of claim 1 of the Lanxess patent. Since the iron sludge pellets are outside the scope of claim 1, also the use claims can be considered irrelevant for the commercialization of the iron sludge pellets.



In conclusion, I have the opinion that the iron sludge pellets as described above do not fall within the scope of the claims of EP- B1-1582505.

Yours faithfully,

Jeannette Verbart,
European patent attorney

Claims(16)

Granules consisting essentially of iron oxide and/or iron oxyhydroxide which have a turbidity by the turbidity test specified in the description of < 300 FNU, obtainable by the mixture of essentially two components essentially consisting of

1. a base and

2. an Fe(III) solution
wherein, if use is made of an $FeClSO_4$ solution, it is added to the charged base.

Granules according to Claim 1, **characterized in that** the granules have a turbidity by the turbidity test specified in the description of < 200 FNU.

Granules according to Claim 1, **characterized in that** the granules have an abrasion value by the abrasion test specified in the description of < 10%.

Granules according to Claim 3, **characterized in that** the granules have an abrasion value by the abrasion test specified in the description of < 5%, in particular < 1.5%.

Granules according to Claim 1, **characterized in that** the granules have α-, β-, γ- and/or δ-FeOOH phases and/or ferrihydrite phases and also mixed and intermediate phases of the same.

Granules according to Claim 1, **characterized in that** the granules, in addition are solidified with oxides and/or /(oxy)hydroxides of the elements Al, Mg, Ti.

Granules according to Claim 1, **characterized in that** the granules have a water content of < 50%, in particular < 20%.

Granules according to Claim 1, **characterized in that** the granules have a particle size of 0.01 to 5 mm, in particular from 0.1 to 1 mm.

Granules according to Claim 1, **characterized in that** the granules are produced by spray drying and have a particle size of < 0.3 mm, in particular < 0.2 mm.

Granules according to Claim 1, **characterized in that** the granules have a BET surface area measured by the carrier gas method ($He:N_2 = 90:10$) by the one-point method as specified in DIN 66131 (1993) of > 100 m^2/g, in particular > 250 m^2/g.

Granules according to Claim 1, **characterized in that** the granules are flowable by the flow test specified in the description.

Granules according to Claim 1, **characterized in that** the granules have an arsenic adsorption by the arsenic adsorption test of > 55%, in particular >80%.

Granules according to Claim 1, **characterized in that** the granules remove pollutants and/or heavy metals such as phosphates and compounds of antimony, beryllium, selenium, tellurium, sulphur, cyanide and arsenic from flowable media such as gases and/or liquids such as water or wastewater.

Use of the granules according to one or more of Claims 1 to 13 for the removal of pollutants and/or heavy metals such as phosphates and compounds of antimony, beryllium, selenium, tellurium, sulphur, cyanide and arsenic from flowable media such as gases and/or liquids such as water or wastewater.

Use of the granules according to Claim 14 for removing arsenic compounds from water or wastewater.

Use of the granules according to Claim 15 in water treatment systems such as cartridges for removing arsenic compounds from water or wastewater.

Description translated from German

[0001]

The present invention relates to stable adsorbent granules which have a high mechanical stability and the use thereof.

[0002]

Contact and adsorbent granules, including those based on iron oxides and / or iron oxyhydroxides, have already been described. They are mainly used in continuous processes, where they usually are in tower- or column-type units, which are traversed by the medium to be treated, where the outer and inner surface of the granules and the accessible pores, the chemical or physical reaction Find or adsorption processes instead of -. For this purpose cannot be used powdered materials because they compact in the direction of flow of the medium, thereby increasing the flow resistance until the unit becomes blocked.

[0003]

If a unit is cleaned by backwashing, large amounts of the powder are discharged and lost or cause an unacceptable contamination of the waste water.

[0004]

However, the flowing media also exert forces on the granules, which can lead to abrasion and / or movement through to violent agitation of the granules. Thus, the granules collide, and consequently undesirable abrasion. This leads to loss of contact or adsorbent material and contamination of the medium to be treated.

[0005]

Iron oxide and hydroxide-containing adsorbents / catalysts are, for example in the field of water purification or gas purification advantageously be used. In water purification, this means, in horizontal or vertical flow filters or adsorber or by adding to the organic or inorganic phosphorus, arsenic, antimony, sulfur, selenium water to be treated for the deposition of dissolved, suspended or emulsified tellurium, beryllium and cyano and Schwermetallionen- and links from, for example, drinking water, industrial water, process water, industrial, municipal wastewater, pit water, mineral, Christmas, thermal and mineral water and aquarium, garden pond and agricultural water use. Is also possible to use in so-called reactive walls for the deposition of these pollutants from groundwater and leachate heads of contaminated sites such as landfills.

[0006]

When the gas purification means in adsorbers for binding undesirable components such as hydrogen sulfide, mercaptans, and hydrogen cyanide, as well as other phosphorus, arsenic, antimony, sulfur, selenium, tellurium, cyano, and heavy metal compounds in waste gases is used. It is also possible to adsorb gases such as HF, HCl, H_2S, SO_x, NO_x.

[0007]

It is also possible the removal of phosphorus, arsenic, antimony, selenium, tellurium, cyano and heavy metal compounds from waste oils and other contaminated organic solvents.

[0008]

Contact and adsorbent granules based on Eiseoxiden and / or iron oxyhydroxides also be used to catalyze chemical reactions in the gas phase or in the liquid phase.

[0009]

There are also various methods known to remove with the aid of adsorbents, and trace contaminants from aqueous systems.

[0010]

Water treatment Continuous adsorbers are preferably used, which are often pursued in parallel arranged in groups. To free example drinking water from organic impurities, such adsorbers are filled with activated charcoal.

[0011]

As for the removal of pollutants such as arsenic from water, iron oxides and / or iron oxyhydroxides are superior to all other known adsorbents. The adsorption of arsenic compounds by iron hydroxide gel has been known for some time (RW Bunsen, AA Berthold, 2nd ed., Göttingen, 1837).

[0012]

In the /patents/DE4320003A1DE 4320003 A1 a method for the removal of dissolved arsenic hydroxide is described by means of solid iron (III).

[0013]

In WO 02/47811 A1 a process for producing an iron-containing sorption material while increasing its pressure at a temperature below 5 ° C will be described.

[0014]

In /patents/DE4320003A1DE 4320003 A1 and WO 02/47811 A1 is named as adsorbent for a fixed-bed reactor, the use of granular ferric hydroxide. The preparation of the granular ferric hydroxide is via a freeze-conditioning (freeze-drying) of by neutralization of acidic iron (III) salt solutions obtained iron hydroxide at temperatures below minus 5 ° C. This manufacturing process is energy intensive, highly and leads to high salt polluted wastewater. In addition, as a result of this production process, a very broad particle size spectrum also contain very small granules with low mechanical stability. This results when used in a fixed bed reactor to the fact that the size spectrum is significantly reduced by mechanical abrasion of the particles during operation, which in turn results in that finely dispersed particles are discharged from contaminated or uncontaminated adsorption from the reactor. A further disadvantage of these granules is that the adsorption capacity with respect to arsenic compounds is considerably reduced if the granules, for example, lose stored dry for extended time water. If the granules z. B. shipped in a moist state, it tends to stick and is difficult to be conveyed.

[0015]

In addition, the stability of the granules decreases with a high water content, which is particularly noticeable when transporting a negative impact. A high water content also increases the cost of transporting the medium. Moist medium offers an ideal breeding ground for bacteria, which can be washed out during operation in the drinking water. If moist medium in the trade, care must be taken that it is the moisture uncontrolled lost, such as when drying in air or in the sun, otherwise the effect can be lost and the granule size distribution due to shrinkage and bulk density of not more reliable are.

[0016]

Furthermore it is known that aging z. B. amorphous Fe $(OH)_3$ in aqueous media is quicker of furnish as in the dry state. This is associated with crystallization and possibly a reduction in the adsorption capacity and stability.

[0017]

Another disadvantage of this method has proved in practice, the nature of the granular material, because the material is relatively soft and fine-grained. As a result, joins the backwash of the filled with the material filter to a significant loss of material. Therefore, in each backwashing new material needs to be added, whereby the cost for implementing the method is substantially increased. In addition, the water or wastewater to be treated has to be relatively clean, as otherwise occur deposition of solid components of the water on the pellets by the filter effect, and therefore the distance of the desired components is impeded.

[0018]

The in WO 02/26630 A1 and WO 02/26632 A1 iron oxide or described - but hydroxidgranulate are ideal for use in fixed-bed adsorbers. The optional grated from the granules by improper mechanical stress on the granules fines will be held from time to time by backwashing of the bed along with algae, iron flakes and other from groundwater derived fines and is collected in a separate container, and sedimented there. In closed water purification containers, however, such as cartridges or baskets is such a separate washing out the fines, which could contaminate the treated water is not readily available. Closed water purification containers contain the Adsorptionmittel in a bed.

[0019]

As well as granules described the invention may be free from foreign binders, the material is comparatively easy to dispose of after use.

[0020]

However, the stability of compacted powders during extended use in adsorbers is inadequate and in need of improvement. Therefore, these formulations are designed for use in, for example, adsorbers, particularly continuous, in the purification of water under certain conditions into consideration. Especially during maintenance or cleaning of the adsorber by backwashing (s. Below), such granules lose the associated agitation large amounts of substance. The backwash wastewater is heavily clouded by the abrasion. This is unacceptable for several reasons: First of all, is lost adsorber, which is piled high for a longer life with impurities and therefore of toxicological concern. Then the waste stream will be charged abrasion, which can sediment and thus leads to impairment of piping systems and ultimately the WWTP physically and toxicologically undesirable burden, to name just a few reasons.

[0021]

In many cases, one is faced with the problem, especially in regions where wells tap or drinking water contaminated with arsenic general or other heavy metals that have no proper drinking water treatment plant in the vicinity or no suitable aggregate at hand, which remove pollutants continuously would.

[0022]

From the company Brita Water Filter Systems GmbH cartridges and devices for treating liquids are, for example, are known (/patents/DE19905601A1DE 19905601 A1 ;

/patents/DE19915829A1DE 19915829 A1 ; /patents/DE19814008A1DE 19814008 A1 . /patents/DE19615102A1DE 19615102 A1 . DE 4304536 A1 . /patents/US6099728US 6,099,728). These devices are well suited for full- or partial desalination of drinking water in domestic jugs immediately before use of drinking water. However, for ease of handling of the granules in transport, when transferring or charging the adsorber, it is necessary that the granules have a very low moisture content, otherwise they tend to stick and can no longer flow freely.

[0023]

The present invention is therefore an object to produce improved granules based on iron hydroxide, which have a high mechanical stability combined with a high binding capacity contained in liquids and gases pollutants that have free flow and a low water content, and which without organic binders or inorganic foreign binders sufficient mechanical stability Erlangen.

[0024]

This object is achieved by granules consisting essentially of iron oxide and / or iron oxyhydroxide which have a turbidity value by the turbidity test of <300 FNU, available through the mixture of essentially two components consisting essentially of

1. a base and

2. an Fe (III) solution

wherein if a FeClSO used $_4$ solution, it is added to the initial charge of base.

[0025]

The granules preferably have a haze value after the turbidity test of <200 FNU.

[0026]

The granules preferably have an abrasion value after the abrasion test of <10%. Preferably, the granules have an abrasion value by the abrasion test of <5%, most preferably of <1.5% on.

[0027]

The granules of the invention are considerably stronger and thus have a much greater abrasion resistance to mechanical and hydraulic stressing.

[0028]

All known solid adsorbent show even after repeated mechanical stress a continuous wear that leads to an intolerable Rotbis browning of the passing water. For this reason, an abrasion test and a haze test was developed, which carries the real requirements for the stability of the bill adsorbent.

[0029]

The evaluation of the mechanical and hydraulic abrasion resistance made by the following methods: Turbidity test

[0030]

An improved test of granule stability that comes to real requirements in cartridge applications also suggest the turbidity measurement of the supernatant suspension after mechanical agitation of the granules in water. The turbidity measurement is an important process in the water, waste water and sludge.

[0031]

10 g of granules in a 250ml glass bottle "DURAN" with scaling, Messrs. Schott, article no. 21801365 weighed and filled with deionized H_2O to 150ml. Then the bottle in the laboratory shaker "LabShaker" model Kuhner, Messrs. Brown-Melsungen is clamped and shaken at room temperature for 30 min at 250 rpm. This procedure provides a so-called. Abrasion cycle. The bottle contents are then allowed to stand for 1 min (sedimentation) and then decanted through a 200mm circular sieve the Fa. Retsch with 40 microns mesh. The filtrate passed through the sieve is subjected to the turbidity measurement. For measuring turbidity measurement method according to EN ISO 7027: 1999 we used a laboratory turbidimeter "Nephla" from Dr. Lange.. Measurement method: 90 ° light-scattering photometry, wavelength: 860 nm; Balance: DIN standard Formazine; Ambient temperature: 20-25 ° C; The calibration is performed by light scattering of formazine in turbidity units Formazine (TE / F) that are specified in more detail, however, as FNU (formazine nephelometric units). The turbidity value (dimension: = TE / F "turbidity unit Formazine" or FNU = "formazine nephelometric units") is worn around against the number of cycles of abrasion. For the present invention the measurement of the turbidity after the 5th cycle was selected as a feature of the invention. Should only those granules are considered to be abrasion stable in the sense of the turbidity test, do not exceed a certain claimed turbidity

value in each of five succeeding cycles of abrasion. A sample of deionized water with the granules of the invention are brought into contact, for example, has a turbidity 0.37 NTU.

[0032]

The granules of the invention, even after the sharp mechanical loads no abrasion, which leads to an unwanted turbidity of the supernatant solution (Fig. 1). Abrasion test

[0033]

10 g of the examined granulate with grain sizes> 0.5 mm and ≤ 5% moisture contents were placed in a 250ml glass bottle "DURAN" with scaling, Messrs. Schott, article no. 21801365 weighed with 150 ml of deionized water was added and on a shaker LabShaker (Kuhner model, Messrs. Brown-Melsungen) over a period of 30 minutes at 250 revolutions / minute added at room temperature in rotation. Then, <0.1 mm was supported by the suspension using a screen, the fine fraction isolated, ≤ 5% dried to a moisture content and weighed. The weight ratio between product weight and initial weight determines the abrasion value x in%. x (%) = [100 × Weight of fines (g) / initial weight granules (g)].

[0034]

The same results for abrasion and turbidity were achieved when a modern table shaker "Lab-Shaker", Fa. Kuhner AG, type LSR V-25, shaking 250 revolutions / minute with digital frequency display (+/- 1 U / min) was used.

[0035]

The granules preferably have α-, β-, γ- and / or δ- FeOOH phases and / or Ferrihydrit- and mixed and intermediate phases of the same on. The granules are particularly preferably additionally with oxides and / or / (oxy) hydroxides of the elements Al, Mg, Ti solidified.

[0036]

The use of finely divided iron oxyhydroxides invention, for example, transparent iron oxyhydroxide are having a mean particle size of less than 0.1μm and specific surface areas of more than 80 m $^{2.}$ But it can also be used in accordance with finely divided iron oxide pigments, preferably hematite, magnetite or Maghämite.

[0037]

The granules preferably have a water content of <50%, preferably <20%, most preferably <10%. The moisture or water content determined one by drying a sample in a convection oven at 70-100 ° C to constant weight. The difference between initial and final weights determines the moisture content.

[0038]

The grain size of the material is arbitrary, it is preferably between 0.1 and 40 mm, more preferably between 0.2 to 20 mm. This can be achieved by mechanical shaping of the semi-solid, pasty filter cake before drying by a granulating or pelletizing plant or in an extrusion press to form shaped bodies having a size in the range between 0.2 and 20 mm, followed by drying in air on a belt dryer or in a drying oven, and / or. by mechanical comminution to the desired particle size after drying Thereafter, the granules preferably have a particle size of 0.01 to 5 mm, preferably from 0.1 to 1 mm. If the granules prepared by spray-drying, they preferably have a particle size of <0.3 mm, in particular of <0.2 mm. The particle size determination are thereby performed with the Mastersizer the Fa. Malvern Instruments.

[0039]

The granules preferably have a primary particle size of up to 100 nm, preferably from 4 to 50 nm. The primary from scanning electron micrographs is determined by measurement (instrument: XL30 ESEM FEG, Philips.).

[0040]

The granules preferably have a BET Obefläche on of> 100 m ^{2} / g, in particular> 250 m ^{2} / g. The determination of the specific surface area according to BET of the products according to the invention takes place via the carrier gas method (He: N $_2$ = 90: 10) of the one-point method according to DIN 66131 (1993). Before measurement, the sample 1 is heated in a dry nitrogen stream at 140 ° C h.

[0041]

For the ease of use of the granules in transport, when transferring or charging the adsorber, it is also necessary that the granules have a very low moisture content, otherwise they tend to stick and can no longer flow freely. The granules are therefore preferably flowable. The free flowability (flow test) is determined by uniformly a 25 g sample in a Haver & Boecker test sieve shaker type Haver EML200 digital plusN on a DIN round sieve of diameter 200 mm with a mesh size equal to the upper limit of the grain size distribution of the product, distributed and screened by an amplitude of 0.3 mm. Is considered to be flowable when within 1 min granulate is sieved through at least> 95%.

[0042]

Although not defined as a flow test in the sense of the application, you can also see the free flowability of the granules in which one measures the time in which a granule volume of 100 mL, with a DIN flow cup according to DIN EN ISO 2431: 1996, outlet of 8 mm diameter through flows freely until it is completely empty.

[0043]

It has been found that the granules of the invention have a high binding capacity for substances in waters, liquids or gases and pollutants, they also have a sufficiently high resistance to flowing media in terms of mechanical or hydraulic loading.

[0044]

The granules preferably have an arsenic adsorption by the arsenic adsorption test of> 55%, more preferably> 80% at. Arsenic Adsorption

[0045]

To measure the adsorption of arsenic (V) in a 5L are PE bottle for a specified period 3L of an aqueous solution of Na $_2$ HAsO $_4$ at a pH of about 8 with the respectively specified concentration of about 2.5-3 mg / L arsenic treated with 3 g of the sample under investigation and it puts the bottle on rotating rollers at room temperature in motion. After defined time intervals, takes about 50 mL of the solution, it is filtered through a cellulose acetate membrane filter with a pore size of from 0:45 μ, and measures their arsenic content. As the adsorption of ions on iron hydroxide is defined as a concentration of the specified remaining in solution after 120 min As $^{/5+}$ ions, and in the examples in%, compared with the given initial concentration (= 100%)

[0046]

To measure the adsorption of Cd $^{2+}$ and V $^{5+}$ in a 5L are PE bottle for a specified period 3L of an aqueous solution of Cd (NO $_{3) 2}$ and NaVO $_{3,}$ at a pH value of 7.5 with respectively $^{5+}$ treated indicated concentration of approximately 2.4 mg / L of Cd $^{2+}$ or V with 3 g of the sample under investigation, while the bottle on rotating rollers ("roller block") rotated at 60 rev / min at room temperature around its longitudinal axis and it set in motion. After defined time intervals, takes about 50 mL of the solution, it is filtered through a cellulose acetate membrane filter with a pore size of from 0:45 μ, and measures their arsenic content. The adsorption of As ions on iron hydroxide is defined as the content of after 120 min in solution remaining heavy metal ions, and is in the examples in%, compared with the specified initial amount specified (= 100%) in the same manner as in arsenic:

x_1 mg in solution before = 100%;

x_2 mg after 120 min = Y%;

Adsorption after 120 min: Z% Y% = 100%.

[0047]

The As and heavy metal contents of the contaminated iron oxyhydroxide or of the solutions are determined using mass spectrometry (ICP-MS) according to DIN 38406-29 (1999) or via optical emission spectroscopy (ICP-OES) according to EN ISO 11885 (1998) each inductively coupled plasma excitation unit

[0048]

Iron oxyhydroxides with high specific surface areas can in particular be produced with base preferably by reaction of Fe (III) salts. To an acidic Fe $^{3+}$ salt solution (FeCl $_{3,}$ Fe $_2$ SO $_{4) 3,}$ FeClSO $_{4,}$ Fe (NO $_{3) 3}$ or other dissolved salts), according to the stoichiometry of the reaction of Fe $^{3+}$ + 3 OH $^-$ $\rightarrow$ Fe (OH) $_3$ alkali (NaOH, KOH, NH $_{3,}$ Na $_2$ CO $_{3,}$ Ca (OH) $_{2)}$ added until the pH remains stable at pH 6-8, and Fe (OH) $_3$ is precipitated quantitatively. In a preferred embodiment, the Fe (III) salt solution only up to an acidic pH (particularly preferred: pH4-7) like so that Fe is not yet precipitated quantitatively, since the adsorption properties of the medium improved slightly acidic pH , The reactions described above can of course be carried out in the reverse order of addition, with the exception of FeClSO $_4$ solution, and the acidic pH can be adjusted by an excess of Fe ^{3} + salts.

[0049]

In the precipitation processes in aqueous medium under the existing knowledge that precipitations in an alkaline medium to less adsorbent granules than those in an acid. For example, by concentration and temperature, an aging Fe (OH) $_3$ can be selectively controlled to crystalline FeOOH phases.

[0050]

Depending on the reaction conditions, the phases δ-FeOOH, β-FeOOH, α-FeOOH can be obtained ferrihydrite, which may have very high surface areas, depending on the degree of crystallinity and therefore very good adsorb arsenic.

[0051]

In poorly crystalline phases, the Röntgenpulverdiffiaktogramm shows broad reflections and in electron micrographs of a dispersed granule sample finely divided particles in diameter can be seen from several nanometers.

[0052]

The finely divided iron hydroxide used has an irregular particle morphology. In the scanning electron micrographs can usually see heaps of agglomerated, in part spherulitic particles. These individual particles have a diameter of about 50 nm. The BET surface area ranges from 50 to 500 m^2 / g, preferably from 150 to 350 m^2 / g.

[0053]

The primary particle size was obtained from scanning electron micrographs is determined by measurement (instrument: XL30 ESEM FEG, Philips.). If the primary acicular such. As in the phase of α-FeOOH, can be used as a measure of the particle size of the needle width can. Observed in α-FeOOH particles nanoparticulate needle widths of up to 100 nm, in the main, however, between 4 and 50 nm by doping or special reaction, the needle shapes can in their length. Vary width ratio. If the primary particles are isometric, such. As in the phases of ferrihydrite, δ-FeOOH, $\alpha\text{-}Fe_2O_3$, $\gamma\text{-}Fe_2O_3$, the particle diameter may be even smaller than 20 nm well.

[0054]

As is apparent from XRD powder patterns, the iron oxide-hydroxide may be substantially amorphous or contain ferrihydrite structures.

[0055]

From the thus-prepared suspension of iron hydroxide compounds, the water containing dissolved components can be removed in several ways. The simplest version, the complete removal of water from the suspension, for. Example by spray drying and subsequent washout of crystallized salts by redispersion of the solid mixture, followed by filtration, paste formation and / or granulation and drying has been found.

[0056]

For applications where higher demands on the mechanical strength of the granules / contacts are made, the suspension is filtered or centrifuged and the residue washed essentially salt-free. It has been found that the stability of the granulates described still have sufficient stability even in a foreign salt content of up to 5%. The (filter) cake which is obtained as residue is a solid to semisolid paste. These can then be drained completely or partially, and the material thus obtained can then be cut into the desired shape and / or size. The subsequent application of the granules determines the preferred procedure in its preparation and is determined by the person skilled in the particular field of application by simple preliminary experiments. Both the directly dried filter cake and the dried shaped bodies can then be used as contact or adsorbent.

[0057]

As another method of producing granules Granulation of a semi-wet paste has proven itself. It is molded pellets or strands of a semi-solid paste z. B. by means of a simple perforated plate, a roller press or an extruder, and either dried immediately or brings these extrudates using a granulator, in addition to a spherical or granular form. The still moist beads or granules can subsequently be dried to any moisture content. To prevent the granules clump together, a residual moisture content recommended by <50%, preferably <30%, more preferably <20%.

[0058]

By spray can for example very finely divided granules produce that provide a very high outer contact surface. At the outer grain surfaces are the first contacts with the dissolved ions instead. Although find diffusion and adsorption of ions in the pores and channels of the granules take place, but only after a certain contact time.

[0059]

Because of their high density and abrasion stability, the spray granules can be employed without significant pressure loss in a filter system, the z. B. can also be operated in upflow. However, a preferred application of these granules is to use in cartridge housings that have a high adsorption capacity for arsenic and other contaminants at very short contact times, but must at the same time guarantee a high abrasion safety.

[0060]

A spherical shape and a uniform particle shape can be designed for use in fixed-bed adsorbers due to the improved packing in the adsorber vessel against irregular rough-ground granules or pellets in rod form.

[0061]

Generally, it is possible to improve the filtration behavior of the suspensions apply conventional filtration-enhancing measures such as those in Solid-Liquid Filtration and Separation Technology, A. Rushton, AS, Ward RG Holdich, 2nd ed. 2000, Wiley-VCH, Weinheim, and Commission Industiellen solid / liquid filtration, H. Gasper, D. Oechsle, E. Pongratz, 2nd ed. 2000 Wiley-VCH Weinheim are described. Thus, the suspensions can be added, for example a flocculant.

[0062]

The products of this invention can undergo drying in air, and / or in vacuo and / or in a drying oven and / or belt dryers or by spray drying, preferably at temperatures from -25 to 250 ° C, particularly preferably at 60 to 120 C, are subjected. Drying is conveniently at temperatures up to 250 ° C. A vacuum or freeze-drying of the material is possible.

[0063]

The products of the invention preferably have a residual water content of less than 50 wt .-%.

[0064]

According to the above-described methods available products can then be comminuted, for example by crushing or grinding on. Since the products on their first contact with water, such as when first filling a freshly charged adsorber with water, but crush autogenous, this will not be necessary as a rule. This results in a random particle-size distribution, but no particles of a size that will take place to any significant extent by the flowing medium from the adsorber.

[0065]

A separate granulation as (flowable) powder would be required when using conventional iron oxyhydroxides in the form, either with the aid of foreign binders or using extremely high linear forces during compacting can be dispensed with entirely.

[0066]

The invention also relates to the use of the granules remove pollutants and / or heavy metals such as phosphates, antimony, beryllium, selenium, tellurium, sulfur cyan and arsenic compounds from flowable media such as gases and / or liquids such as water or wastewater , Also Geruchststoffe be adsorbed.

[0067]

The granules are particularly preferably used for removing arsenic compounds from water or wastewater.

[0068]

Using numerous experiments it was shown that are adsorbed by the granules according to the invention also with arsenic ions isostructural ions such as. For example, phosphate, antimonate, molybdate, chromate, tungstate, vanadate.

[0069]

A preferred in this technical field is the decontamination of water, in particular drinking water. More recently, the removal of arsenic from drinking water given special attention. The granules of the invention suitable for this purpose perfectly, since even the low set by the US EPA limits the use of the granules of the invention are not only met, but can even be exceeded.

[0070]

The granules are preferably used in water-processing facilities such as cartridges for the removal of arsenic from water or wastewater.

[0071]

The examples below the invention is illustrated, without thereby limiting the invention to be effected. **Examples** **Example 1**

[0072]

There were 76 m ^{3} solution with 107 g / l of Fe $_2$ (SO $_{4)}$ heated $_3$ 50 ° C and subsequently min in 61 to 15m ^{3} NaOH solution (300 g / L) while gassing with 1500 m ^{3} / h of air to a final pH of 9.2. After the addition was complete, the mixture stirred for 22 min was under fumigation. The mixture was washed <1000 ĩS / cm on a filter to a filtrate conductivity, hold the filter through a paste Molder belt dryer and dried. The particle fraction 0.5-2 mm was studied.
BET: 326 m ^{2} / g
Wear (abrasion test): 2.4%;
Turbidity (cloudiness test) after 2 passes: 250 FNU;
Turbidity (cloudiness test) after 5 rounds: 135 FNU;

Water content: 9%;
Bulk density: 0.94 g / cm $^{3;}$
Phase analysis: main component = FeOOH.
As (V) adsorption after 120 min: 59.3%;
Cd $^{2+}$ adsorption after 120 min: 54.2%; $_0$ c = 2.4 mg / L; C (120 min) = 1.1 mg / L.
V $^{5+}$ adsorption after 120 min: 33.3%; $_0$ c = 2.4 mg / L; C (120 min) = 1.6 mg / L.
Flow test: flows. **Example 1A**

[0073]

A portion of the washed filter paste was spray-dried using a 0.8 mm nozzle. This resulted in a very narrow particle size distribution mainly between 30 and 200 microns: D (v, 0.1) = 58.97 microns; D [3,2] = 91.36 .mu.m.
BET: 326 m ^{2} / g.
Turbidity (cloudiness test) after 2 passes: 28 FNU;
Turbidity (cloudiness test) after 5 rounds: 16 FNU;
Water content: 22.3%;
Bulk density: 1.00 g / cm $^{3;}$
As (V) adsorption after 120 min: 96.4%;
Flow test: flows.

Example	As content in the filtrate [g / l] for x min contact time						
	Exit	5min	10min	30min	60min	120min	360min
Example 1	2700	2300	2200	1800	1400	1100	510
Example 1A	2500	1500	960	440	180	90	30

Example 2

[0074]

There were 76 m ^{3} solution with 106.3 g / l of $Fe_2(SO_4)_3$ was heated to 45 ° C and then 50 min with approx 13m ^{3} NaOH solution while gassing with 1500 m ^{3} / h of air to final pH 4.7 like. After the addition was complete, the mixture was stirred for 28 min under fumigation. Part of the batch was washed <1000 ĩS / cm on a filter to a filtrate conductivity, down the filter through a paste former (with 6.5mm perforated sheet) onto a belt dryer and dried. The particle fraction 0.5-2 mm was studied.
BET: Final sample: 185 m ^{2} / g;
Abrasion value (abrasion test): 4.7%;
Water content: 6.0%;
Bulk density: 0.94 g / cm $^{3;}$
As (V) adsorption after 120 min: 63.0%;
Phase analysis: main component = FeOOH;
Flow test: flows. **Example 2A**

[0075]

A portion of the washed filter paste was mashed to a suspension of 9.5% solids and dried on a nozzle spray dryer with 0.8mm nozzle.
BET: 326 m ^{2} / g.
Water content: 16.9%;
Bulk density: 1.08 g / cm $^{3;}$
Turbidity (cloudiness test) after 2 passes: 276 FNU;
Turbidity (cloudiness test) after 5 rounds: 76 FNU;
As (V) adsorption after 120 min: 98.8%;
V $^{5+}$ adsorption after 120 min: 54.2%; $_0$ c = 2.4 mg / L; C (120 min) = 1.1 mg / L.
Flow test: flows.

Example	As content in the filtrate [g / l] for x min contact time						
	Exit	5min	10min	30min	60min	120min	360min
Example 2	2700	2400	2200	1800	1400	1000	290
Example 2A	2700	1800	1400	740	280	70	<10

Example 3:

[0076]

7.5 L of NaOH solution (100 g / L) are charged, heated with stirring to 70 ° C and 30 min with 13.5 L of a $FeClSO_4$ solution (100 g / L) to pH 5. The mixture was stirred for 30 min. A 5 L suspension is washed on the filter until a conductivity of <1000 ĩS / cm and then dried at 75 ° C. The dried solids are forced through a 2 mm sieve, the fines are sieved <0.5 mm.
BET: 304 m ^{2} / g;
Abrasion value (abrasion test): 1.1%
Turbidity (cloudiness test) after 2 passes: 167 FNU;

Turbidity (cloudiness test) after 5 rounds: 152 FNU;
Water content: 11.4%;
Bulk density: 1.00 g / cm $^{3;}$
As (V) adsorption after 120 min: 64.3%;
Flow test: flows;
Phase: possibly poorly crystallized δ-FeOOH.

	As content in the filtrate [g / l] for x min contact time					
	Exit	5min	10min	30min	60min	120min	360min
Example 3	2800	2500	2300	1800	1500	1000	240

Example 4

[0077]

12.2 L of Fe $_2$ (SO $_{4)}$ submitted $_3$ solution (107 g / L), heated with stirring to 70 ° C and 30 min with 9.0 L of NaOH solution (100 g / L) was added to pH 5. The mixture was stirred for 30 min. A 5 L suspension is washed on the filter until a conductivity of <1000 ĩS / cm and then dried at 75 ° C. The dried solids are forced through a 2 mm sieve, the fines are sieved <0.5 mm.
BET: 312 m ^{2} / g;
Abrasion value (rubbing test): 0.7%
Turbidity (cloudiness test) after 2 passes: 135 FNU;
Turbidity (cloudiness test) after 5 rounds: 139 FNU;
Water content: 12.7%;
Bulk density: 0.89 g / cm $^{3;}$
As (V) adsorption after 120 min: 81.4%;
Flow test: flows;
Phase: X-ray amorphous.

	As content in the filtrate [ug / 1] after x min contact time						
	Exit	5min	10min	30min	60min	120min	360min
Example 4	2800	2500	2100	1600	1100	520	60

Example 5 (Comparative Example)

[0078]

It 956 l of deionized water were introduced into the stirred reactor with stirring 280 kg of FeClSO $_4$ solution (with 40.73% FeClSO $_{4)}$ were then added and the solution heated to 50 ° C. The solution with NaOH (100 g / L) to pH 5.0 with 25-30 kg / min) and like 30 minutes. stirred. The suspension was washed on a filter press to a conductivity of <1000 S / cm and then dried in a convection oven at 75 ° C. The dried solids are forced through a 2 mm sieve, the fines are sieved <0.5 mm.
BET: 334 m ^{2} / g;
Abrasion value (abrasion test): 3.6%
Turbidity (cloudiness test) after 2 passes: 219 FNU;
Turbidity (cloudiness test) after 5 rounds: 330 FNU;
Water content: 6.5%;
Bulk density: 0.51 g / cm $^{3;}$
As (V) adsorption after 120 min: 97.3%; Flow test: flows;
Phase: possibly poorly crystallized δ-FeOOH.

	As content in the filtrate [g / l] for x min contact time						
	Exit	5min	10min	30min	60min	120min	360min
Example 5	2600	1900	1700	950	430	70	10

Summary Table

[0079]

Example	**1**	**1A**	**2**	**2A**	**3**	**4**	**5**
BET m ^{2} / g	326	326	185	326	304	312	334
Abrasion in% after the abrasion test	2.4	-	4.7	-	1.1	0.7	3.6
Water content in%	9	22.3	6.0	16.9	11.4	12.7	6.5
Bulk density in g / cm ^{3}	0.94	1.00	0.94	1.08	1.00	0.89	0.51
As adsorption (% after 120 min)	59.3	96.4	63.0	98.8	64.3	81.4	97.3
Turbidity FNU after 2 passes (turbidity test)	250	28	-	276	167	135	219
Turbidity FNU after 5 cycles (turbidity test)	135	16		76	152	139	330
Turbidity FNU after 6 runs (turbidity test)	148	11	-	53	135	109	304

Turbidity FNU after 7 runs (turbidity test)	126	13	-	62	134	120	322
Turbidity FNU after 8 passes (turbidity test)	136	13	-	54	149	103	478
Turbidity FNU by 9 runs (turbidity test)	120	13	-	47	151	95	417
Turbidity FNU by 10 runs (turbidity test)	124	9	-	44	134	85	489
Flow test: flows (Yes or No)	Yes	Yes	Yes	Yes	Yes	Yes	Yes

[0080]

Fig. 1 shows the turbidity measurement of the supernatant solution with increasing abrasion cycles after the turbidity test. The y-axis shows the turbidity unit [NTU], while the x-axis represents the runs. The curves for Commercial Bayoxide ® E33 are as A, B as Example 1, Example 1A as C, D as Example 2A, Example 3 as E, indicated as F Example 4 and Comparative Example 5 as G. Fig. 1 shows that Bayoxide ® E33 always an abrasion value and therefore a turbidity at very high levels, while granules of the invention show a very low opacity. The products of the invention are mentioned as examples.

Referenced by

Citing Patent	Filing date	Publication date	Applicant	Title
DE102010020820A1	May 18, 2010	Nov 24, 2011	Crenox Gmbh	Adsorptionsmittel enthaltend Titan- und Eisenverbindungen
WO2011144637A1	May 17, 2011	Nov 24, 2011	Crenox Gmbh	Adsorbing agent containing titanium and iron compounds

Classifications

International Classification	C02F1/28, C01G49/02, B01J20/06
Cooperative Classification	Y02W10/37, Y10S210/912, C02F1/281, B01J20/06, C02F2101/20, B01J20/0229, C02F2101/18, C02F2101/103, C02F1/288, B01J20/28061
European Classification	B01J20/02B12B, C02F1/28B, B01J20/28F4D, B01J20/06

Legal Events

Date	Code	Event	Description
Oct 5, 2005	AX	Request for extension of the european patent to	Countries concerned: ALBAHRLVMKYU
Oct 5, 2005	AK	Designated contracting states:	Kind code of ref document: A1 Designated state(s): AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR
May 31, 2006	17P	Request for examination filed	Effective date: 20060405
Jun 14, 2006	AKX	Payment of designation fees	Designated state(s): AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR
Feb 21, 2007	17Q	First examination report	Effective date: 20070119
Jun 25, 2008	AK	Designated contracting states:	Kind code of ref document: B1 Designated state(s): AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR
Jun 25, 2008	REG	Reference to a national code	Ref country code: GB Ref legal event code: FG4D Free format text: NOT ENGLISH
Jul 31, 2008	REG	Reference to a national code	Ref country code: CH Ref legal event code: EP
Aug 7, 2008	REF	Corresponds to:	Ref document number: 502005004490 Country of ref document: DE Date of ref document: 20080807

			Kind code of ref document: P
Aug 20, 2008	REG	Reference to a national code	Ref country code: IE Ref legal event code: FG4D Free format text: LANGUAGE OF EP DOCUMENT: GERMAN
Oct 31, 2008	PG25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: SI Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625 Ref country code: FI Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625
Nov 28, 2008	PG25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: FI Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625 Ref country code: PL Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625 Ref country code: NL Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625
Dec 1, 2008	REG	Reference to a national code	Ref country code: ES Ref legal event code: FG2A Ref document number: 2308326 Kind code of ref document: T3
Dec 31, 2008	PG25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: NL Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625
Jan 5, 2009	NLV1	Nl: lapsed or annulled due to failure to fulfill the requirements of art. 29p and 29m of the patents act	
Jan 28, 2009	REG	Reference to a national code	Ref country code: HU Ref legal event code: AG4A Ref document number: E003967 Country of ref document: HU
Jan 30, 2009	PG25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: LT Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625 Ref country code: IS Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20081025 Ref country code: PT

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Feb 4, 2009	REG	Reference to a national code	Ref country code: IE Ref legal event code: FD4D
Feb 27, 2009	PG25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: SK Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625 Ref country code: RO Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625 Ref country code: IS Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20081025 Ref country code: PT Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20081125 Ref country code: LT Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625 Ref country code: CZ Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625
Mar 31, 2009	PG25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: RO Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625 Ref country code: SK Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625

Apr 30, 2009	PG FP	Postgrant: annual fees paid to national office	Ref country code: HU Payment date: 20090311 Year of fee payment: 05
Apr 30, 2009	PG 25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: BG Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080925 Ref country code: IE Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625 Ref country code: DK Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625 Ref country code: EE Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625
May 29, 2009	PG 25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: BG Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080925 Ref country code: IE Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625
Jun 3, 2009	26 N	No opposition filed	Effective date: 20090326
Jun 30, 2009	PG FP	Postgrant: annual fees paid to national office	Ref country code: GB Payment date: 20090325 Year of fee payment: 05
Jul 31, 2009	PG FP	Postgrant: annual fees paid to national office	Ref country code: ES Payment date: 20090428 Year of fee payment: 05
Aug 31, 2009	PG FP	Postgrant: annual fees paid to national office	Ref country code: IT Payment date: 20090318 Year of fee payment: 05 Ref country code: DE Payment date: 20090319 Year of fee payment: 05
Sep 30, 2009	PG FP	Postgrant: annual fees paid to national office	Ref country code: BE Payment date: 20090401 Year of fee payment: 05
Oct 30, 2009	PG FP	Postgrant: annual fees paid to national office	Ref country code: FR Payment date: 20090316 Year of fee payment: 05
Oct 30,	PG 25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: MC Free format text: LAPSE BECAUSE OF NON-PAYMENT OF

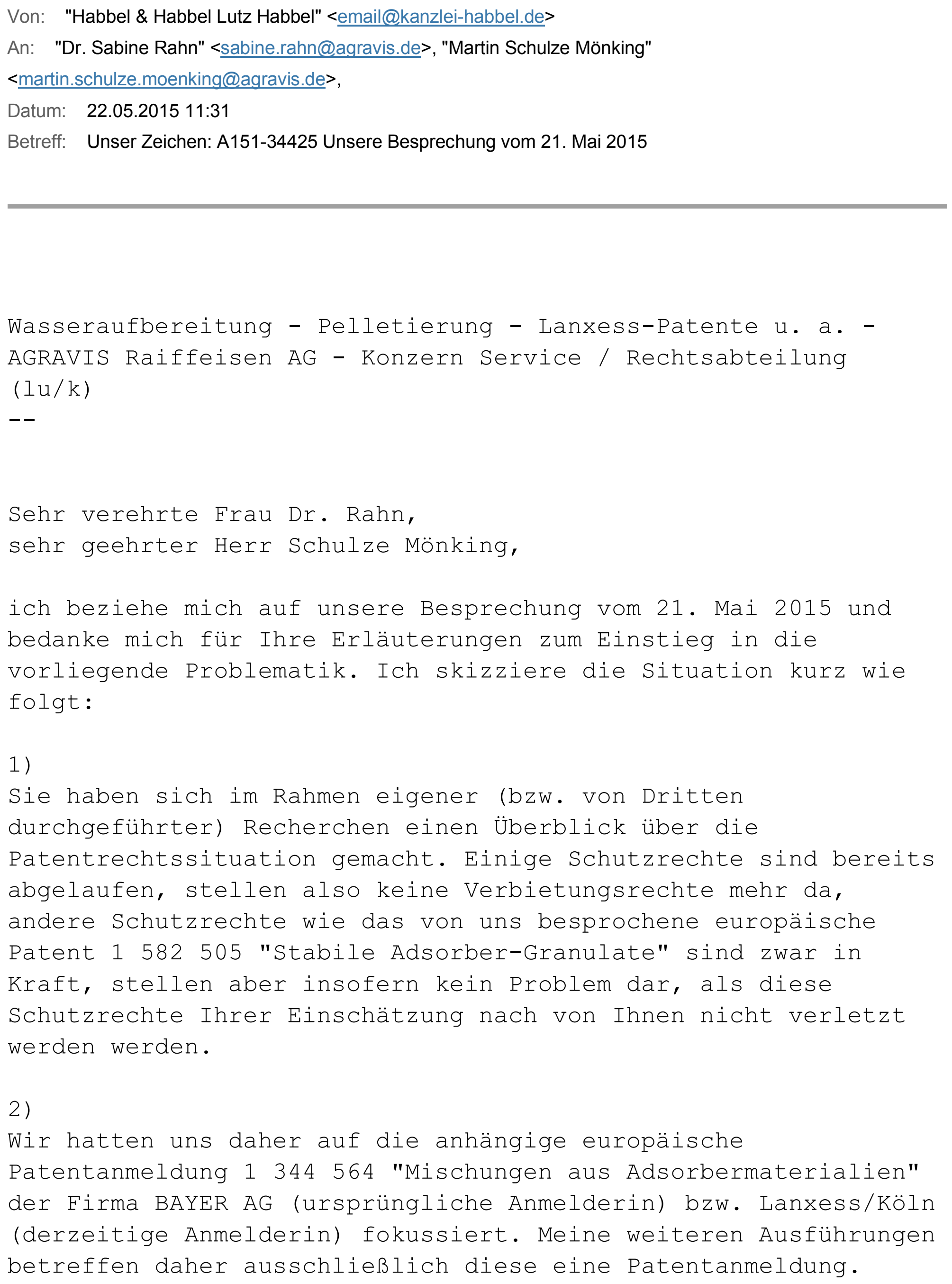
2009			DUE FEES Effective date: 20090331
Oct 30, 2009	REG	Reference to a national code	Ref country code: CH Ref legal event code: PL
Jan 29, 2010	PG25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: LI Free format text: LAPSE BECAUSE OF NON-PAYMENT OF DUE FEES Effective date: 20090331 Ref country code: CH Free format text: LAPSE BECAUSE OF NON-PAYMENT OF DUE FEES Effective date: 20090331
Apr 30, 2010	PGFP	Postgrant: annual fees paid to national office	Ref country code: HU Payment date: 20100312 Year of fee payment: 06
May 31, 2010	PGFP	Postgrant: annual fees paid to national office	Ref country code: IT Payment date: 20100320 Year of fee payment: 06 Ref country code: FR Payment date: 20100324 Year of fee payment: 06
Jun 30, 2010	PGFP	Postgrant: annual fees paid to national office	Ref country code: GB Payment date: 20100322 Year of fee payment: 06
Jun 30, 2010	PG25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: AT Free format text: LAPSE BECAUSE OF NON-PAYMENT OF DUE FEES Effective date: 20090326
Jul 30, 2010	PGFP	Postgrant: annual fees paid to national office	Ref country code: ES Payment date: 20100408 Year of fee payment: 06
Aug 31, 2010	PGFP	Postgrant: annual fees paid to national office	Ref country code: DE Payment date: 20100429 Year of fee payment: 06 Ref country code: BE Payment date: 20100322 Year of fee payment: 06
Oct 29, 2010	PG25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: GR Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080926
Nov 30, 2010	PG25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: GR Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080926
Apr 29, 2011	PG25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: LU Free format text: LAPSE BECAUSE OF NON-PAYMENT OF DUE FEES Effective date: 20090326
Apr 29,	PGFP	Postgrant: annual fees paid to national office	Ref country code: HU Payment date: 20110316

2011			Year of fee payment: 07
May 31, 2011	PG FP	Postgrant: annual fees paid to national office	Ref country code: FR Payment date: 20110317 Year of fee payment: 07
Jul 29, 2011	PG FP	Postgrant: annual fees paid to national office	Ref country code: ES Payment date: 20110414 Year of fee payment: 07 Ref country code: GB Payment date: 20110323 Year of fee payment: 07 Ref country code: BE Payment date: 20110311 Year of fee payment: 07 Ref country code: DE Payment date: 20110323 Year of fee payment: 07
Aug 31, 2011	PG 25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: TR Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625
Sep 30, 2011	PG FP	Postgrant: annual fees paid to national office	Ref country code: IT Payment date: 20110323 Year of fee payment: 07
Sep 30, 2011	PG 25	Lapsed in a contracting state announced via postgrant inform. from nat. office to epo	Ref country code: CY Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625 Ref country code: TR Free format text: LAPSE BECAUSE OF FAILURE TO SUBMIT A TRANSLATION OF THE DESCRIPTION OR TO PAY THE FEE WITHIN THE PRESCRIBED TIME-LIMIT Effective date: 20080625
Apr 30, 2012	PG FP	Postgrant: annual fees paid to national office	Ref country code: HU Payment date: 20120314 Year of fee payment: 08 Ref country code: FR Payment date: 20120319 Year of fee payment: 08
Jun 29, 2012	PG FP	Postgrant: annual fees paid to national office	Ref country code: BE Payment date: 20120328 Year of fee payment: 08 Ref country code: GB Payment date: 20120321 Year of fee payment: 08 Ref country code: IT Payment date: 20120321 Year of fee payment: 08
Jul 31, 2012	PG FP	Postgrant: annual fees paid to national office	Ref country code: DE Payment date: 20120411 Year of fee payment: 08
Dec	PG	Postgrant: annual fees paid to national office	Ref country code: ES

31, 2012	FP		Payment date: 20120419 Year of fee payment: 08
Apr 30, 2013	PGFP	Postgrant: annual fees paid to national office	Ref country code: ES Payment date: 20130313 Year of fee payment: 09 Ref country code: DE Payment date: 20130320 Year of fee payment: 09 Ref country code: HU Payment date: 20130313 Year of fee payment: 09 Ref country code: FR Payment date: 20130325 Year of fee payment: 09 Ref country code: GB Payment date: 20130320 Year of fee payment: 09
Jul 31, 2013	PGFP	Postgrant: annual fees paid to national office	Ref country code: BE Payment date: 20130312 Year of fee payment: 09
Jan 2, 2014	REG	Reference to a national code	Ref country code: DE Ref legal event code: R081 Ref document number: 502005004490 Country of ref document: DE Owner name: LANXESS DEUTSCHLAND GMBH, DE Free format text: FORMER OWNER: LANXESS DEUTSCHLAND GMBH, 51373 LEVERKUSEN, DE Effective date: 20131113
Feb 8, 2016	REG	Reference to a national code	Ref country code: FR Ref legal event code: PLFP Year of fee payment: 12
Apr 29, 2016	PGFP	Postgrant: annual fees paid to national office	Ref country code: ES Payment date: 20160211 Year of fee payment: 12 Ref country code: DE Payment date: 20160322 Year of fee payment: 12
May 31, 2016	PGFP	Postgrant: annual fees paid to national office	Ref country code: GB Payment date: 20160323 Year of fee payment: 12 Ref country code: FR Payment date: 20160208 Year of fee payment: 12 Ref country code: BE Payment date: 20151223 Year of fee payment: 12 Ref country code: HU Payment date: 20160225 Year of fee payment: 12
Aug 31, 2016	PGFP	Postgrant: annual fees paid to national office	Ref country code: IT Payment date: 20160324 Year of fee payment: 12

Appendix II Prior art study in Germany

Evaluation by Habbel and Habbel



Von: "Habbel & Habbel Lutz Habbel" <email@kanzlei-habbel.de>
An: "Dr. Sabine Rahn" <sabine.rahn@agravis.de>, "Martin Schulze Mönking"
<martin.schulze.moenking@agravis.de>,
Datum: 22.05.2015 11:31
Betreff: Unser Zeichen: A151-34425 Unsere Besprechung vom 21. Mai 2015

Wasseraufbereitung - Pelletierung - Lanxess-Patente u. a. -
AGRAVIS Raiffeisen AG - Konzern Service / Rechtsabteilung
(lu/k)
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Sehr verehrte Frau Dr. Rahn,
sehr geehrter Herr Schulze Mönking,

ich beziehe mich auf unsere Besprechung vom 21. Mai 2015 und bedanke mich für Ihre Erläuterungen zum Einstieg in die vorliegende Problematik. Ich skizziere die Situation kurz wie folgt:

1)
Sie haben sich im Rahmen eigener (bzw. von Dritten durchgeführter) Recherchen einen Überblick über die Patentrechtssituation gemacht. Einige Schutzrechte sind bereits abgelaufen, stellen also keine Verbietungsrechte mehr da, andere Schutzrechte wie das von uns besprochene europäische Patent 1 582 505 "Stabile Adsorber-Granulate" sind zwar in Kraft, stellen aber insofern kein Problem dar, als diese Schutzrechte Ihrer Einschätzung nach von Ihnen nicht verletzt werden werden.

2)
Wir hatten uns daher auf die anhängige europäische Patentanmeldung 1 344 564 "Mischungen aus Adsorbermaterialien" der Firma BAYER AG (ursprüngliche Anmelderin) bzw. Lanxess/Köln (derzeitige Anmelderin) fokussiert. Meine weiteren Ausführungen betreffen daher ausschließlich diese eine Patentanmeldung.

3)
Die Anmeldung wurde ursprünglich von der Firma BAYER AG eingereicht. Sie ist zunächst auf LANXESS / Leverkusen und mittlerweile übertragen worden auf die Firma Lanxess / Köln.

Die Patentansprüche sind während des Anmelde- und Prüfungsverfahrens überarbeitet worden. Ich füge Ihnen in der Anlage Kopie einer Akteneinsicht bei, in welcher ich einige mir relevant erscheinende Auszüge aus der Anmeldeakte des Europäischen Patentamts beschafft habe. Da Ihnen die ursprünglich eingereichten Unterlagen vorliegen (in Form der veröffentlichten Europäischen Patentanmeldung), habe ich mich auf die dann anschließende Korrespondenz beschränkt.

Die Sortierung ist dabei in chronologisch absteigender Folge, d. h Seite 1 stellt die jüngste Korrespondenz dar und dann wird es immer älter. Die letzten Seiten in diesem Aktenauszug zeigen die Unterlagen zum europäischen Recherchenbericht, den wir kurz angesprochen hatten. Chronologisch fast am Ende (= Seiten 2 ff. der beigefügten pdf-Datei) findet sich die jüngste Eingabe der Patentanmelderin mit den überarbeiteten, derzeit geltenden Patentansprüchen. Der chronologisch letzte (= Seite 1) Eintrag dieses Aktenauszuges betrifft die Mitteilung des Europäischen Patentamts über die jüngste Inhaber-Umschreibung.

4)
Bei Durchsicht der nun anhängigen Anspruchsfassung hatten wir festgestellt, dass zwei unabhängige Ansprüche zu beachten sind: Anspruch 1 betrifft das Herstellungsverfahren und Anspruch 7 die Adsorbermischung. Wie der zuständige Prüfer auf diese Anspruchsfassung reagiert, ist noch nicht bekannt. Momentan können wir nur diskussionshalber davon ausgehen, dass das Patent mit dieser Anspruchsformulierung erteilt werden würde.

Zusätzlich gibt es noch einen interessanten Anspruch 6, der zwar ebenfalls an das Verfahren des Anspruchs 1 angebunden ist, der aber, was die Zusammensetzung der Adsorbermischung betrifft, etwas weiter gefasst ist als Anspruch 7, denn im ersten Aufzählungspunkt des Anspruchs 6 ist ausgeführt, dass lediglich eines der drei dort erwähnten Produkte in der Adsorbermischung enthalten soll, während im Anspruch 7 nur eine solche Adsorbermischung schützt, in der sämtliche drei Produkte vorliegen. Ich schließe allerdings nicht aus, dass es sich im Anspruch 7 um einen redaktionellen Fehler handelt, so dass dessen Formulierung möglicherweise noch an die des Anspruchs 6 angeglichen werden wird, was einerseits den Schutzbereich des Patentanspruchs 7 erweitern würde, allerdings den Anspruch 7 auch stärker angreifbar machen würde, weil dementsprechend leichter neuheitsschädliches, vorveröffentlichtes Material aufgefunden werden kann.

5)
Zum Verfahrensanspruch 1 hatten Sie vorgeschlagen, mir eine detaillierte Auflistung der Verfahrensschritte zuzuleiten, die bei dem von Ihnen geplanten Herstellungsverfahren angewendet werden würden. Ich könnte dann einen Vergleich mit dem im Anspruch 1 der Patentanmeldung beschriebenen Verfahren durchführen um festzustellen, ob ein Verletzungsproblem besteht oder ob gute Aussichten bestehen, vom Patent frei zu sein, wenn das Patent in der uns vorliegenden Fassung der Patentansprüche erteilt werden würde.

6)
Was die Materialmischung nach Anspruch 7 angeht, so waren Sie der Auffassung, dass eine solche Materialmischung seit Jahren und Jahrzehnten bekannt sei. Um den entsprechenden Nachweis führen zu können, wollten Sie nach Veröffentlichungen suchen, also nach einem Stand der Technik, welcher der Öffentlichkeit zugänglich ist und die im Anspruch 7 beschriebene Materialmischung beschreibt. In diesem Fall wäre der Inhalt des Anspruchs 7 zum Prioritätszeitpunkt 12.03.2002 nämlich nicht neu gewesen. Neuheit ist eine wesentliche Voraussetzung für die Rechtsbeständigkeit eines Patents.

Dabei ist zur zeitlichen Relevanz zu beachten, dass die vorliegende europäische Patentanmeldung zwar (erst) im März 2003 angemeldet worden ist, sich jedoch auf eine deutsche Erstanmeldung aus dem März 2002 bezieht. Dieses ältere so genannte Prioritätsdatum vom 12.03.2002 gilt es zu schlagen, d. h., die von uns vorzulegenden öffentlich zugänglichen Nachweise müssen vom 11.03.2002 oder früher datieren.

7)
Kurz zusammengefasst waren wir bei unserer Besprechung der Hoffnung, das Verfahren gemäß Anspruch 1 umgehen zu können, und zum Anspruch 7 den Nachweis führen zu können, dass dieser Anspruch nicht rechtsbeständig ist, sondern sein Inhalt vorveröffentlicht ist. Aus diesen zwei unterschiedlichen Herangehensweisen an die beiden unabhängigen Ansprüche der europäischen Patentanmeldung ergeben sich auch sehr unterschiedliche Konsequenzen:

8)
Dadurch, dass die Ansprüche 2 bis 6 stets vom Anspruch 1 abhängig sind, kann keine Patentverletzung vorliegen, wenn man die einzelnen Merkmale der Ansprüche 2 bis 6 verwirklicht, jedoch vom Verfahren abweicht, welches im Anspruch 1 formuliert ist. Im Falle einer solchen Abweichung sind also die Inhalte der Ansprüche 2 bis 6 unbeachtlich.

9)
Anders sieht es bei der Verteidigungsstrategie zum Anspruch 7 aus: Wenn wir nachweisen können, dass eine Materialmischung

gemäß Anspruch 7 bereits früher bekannt war und Anspruch 7 insofern nicht rechtsbeständig ist, kann der Patentinhaber noch auf die vom Anspruch 7 abhängigen Ansprüche hinweisen, also auf die Weiterbildungen einer Materialmischung, wie sie im Anspruch 7 beschrieben ist, wobei diese Weiterbildungen in den folgenden Ansprüchen 8 bis 14 beschrieben sind.

Um eine Verletzungsproblematik möglichst sicher auszuschließen, ist es also erforderlich, entweder auch für die Ansprüche 8 bis 14 nachzuweisen, dass eine jeweilige solche Materialmischung bereits vor dem Prioritätstag der europäischen Patentanmeldung bekannt war, oder nachzuweisen, dass die von Ihnen hergestellte Materialmischung nicht einem dieser Ansprüche 8 bis 14 entspricht, so dass dann dieser betreffende Anspruch nicht verletzt würde.

Deutlich weniger sicher ist eine Verteidigung für den Fall, dass Sie eine Materialmischung nach einem der Ansprüche 8 bis 14 herstellen und wir nicht nachweisen können, dass eine solche Materialmischung vor dem 12.03.2002 öffentlich bekannt war. In diesem Fall könnten wir den betreffenden Anspruch also nicht wegen mangelnder Neuheit angreifen, sondern allenfalls wegen mangelnder "erfinderischer Tätigkeit" (eine weitere wesentliche Voraussetzung für die Rechtsbeständigkeit eines Patents).

10)
Von meiner Seite aus schlage ich vor, die anhängige europäische Patentanmeldung regelmäßig zu überwachen, z. B. durch quartalsmäßige Nachforschung, um den weiteren Verfahrensgang der europäischen Patentanmeldung zu erfassen.

Wir könnten daraus erkennen, ob ggf. die Ansprüche noch einmal überarbeitet werden, oder ob das Europäische Patentamt nun beschließt, das europäische Patent zu erteilen - oder, es zurückzuweisen. Im Falle der Patenterteilung wäre dann der konkrete Anspruchswortlaut, den wir zu beachten hätten, ersichtlich.

Auch anschließend an die Patenterteilung erscheint eine weitere Überwachung des erteilten europäischen Patents zumindest noch für die Dauer der Einspruchsfrist sinnvoll, um zu erfassen, ob nicht möglicherweise von dritter Seite Einspruch gegen das erteilte europäische Patent eingelegt wird. Dies kann nämlich - wenn das Patent nicht unverändert aufrecht erhalten wird, was ebenfalls möglich ist - zum vollständigen Widerruf des Patents führen, oder zu einer Änderung der Patentansprüche und einem dementsprechend geänderten Schutzumfang des Patents.

11)
Schließlich fragten Sie nach einer Abschätzung für den Bearbeitungsaufwand: Mein Stundenhonorar beträgt € 270,00 und ich gehe bei meinem derzeitigen Kenntnisstand davon aus, dass

der Zeitaufwand nicht mehr als 10 Stunden betragen wird. Dies kann sich allenfalls ändern, wenn wir in eine umfangreichere, detailliertere Diskussion zu den Ansprüche 8 bis 14 eintreten müssen, um diese auf ihre Rechtsbeständigkeit zu überprüfen bzw. darauf, ob diese Ansprüche durch Ihr Vorhaben möglicherweise verletzt werden.

Ich hoffe, Ihnen mit den vorliegenden Informationen zunächst weitergeholfen zu haben. Abgesehen von dem Aktenauszug füge ich Ihnen zur Vervollständigung Ihrer Unterlagen auch noch den offiziell herausgegebenen europäischen Recherchenbericht in Form der "A3"- Druckschrift in der Anlage bei sowie die derzeitige Rechtsstandsinformation des Europäischen Patentamts, die wir kurz besprochen hatten und aus welcher der derzeitige Verfahrensstand hervorgeht, sowie schließlich auch noch die Rechtsstandsinformation des Deutschen Patent- und Markenamtes zu dem eingangs erwähnten, uns nicht weiter interessierenden europäischen Patents 1 582 505, welches zwar mit Wirkung für Deutschland momentan in Kraft steht, Ihrer Einschätzung nach jedoch keine Patentverletzungsproblematik birgt.

Ohne weitere Anweisungen von Ihrer Seite werde ich momentan in der vorliegenden Sache nichts weiter unternehmen. Ich sehe vielmehr Ihren Weisungen mit Interesse entgegen und verbleibe

--
Mit freundlichen Grüßen

Lutz Habbel

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(19) **Europäisches Patentamt**
European Patent Office
Office européen des brevets

(11) **EP 1 344 564 A3**

(12) **EUROPÄISCHE PATENTANMELDUNG**

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03.12.2003 Patentblatt 2003/49

(43) Veröffentlichungstag A2:
17.09.2003 Patentblatt 2003/38

(21) Anmeldenummer: **03004282.4**

(22) Anmeldetag: **27.02.2003**

(51) Int Cl.^{7}: **B01J 20/02**, B01J 20/08, B01J 20/28, C02F 1/28, B01J 20/06

(84) Benannte Vertragsstaaten:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PT SE SI SK TR
Benannte Erstreckungsstaaten:
AL LT LV MK RO

(30) Priorität: **12.03.2002 DE 10210786**

(71) Anmelder: **BAYER AG**
51368 Leverkusen (DE)

(72) Erfinder: **Schlegel, Andreas, Dr.**
47800 Krefeld (DE)

(54) **Mischungen aus Adsorbermaterialien**

(57) Die vorliegende Erfindung betrifft Mischungen aus verschiedenen Adsorptionsmaterialien, deren Adsorptionseigenschaften sich in der Mischung ergänzen.

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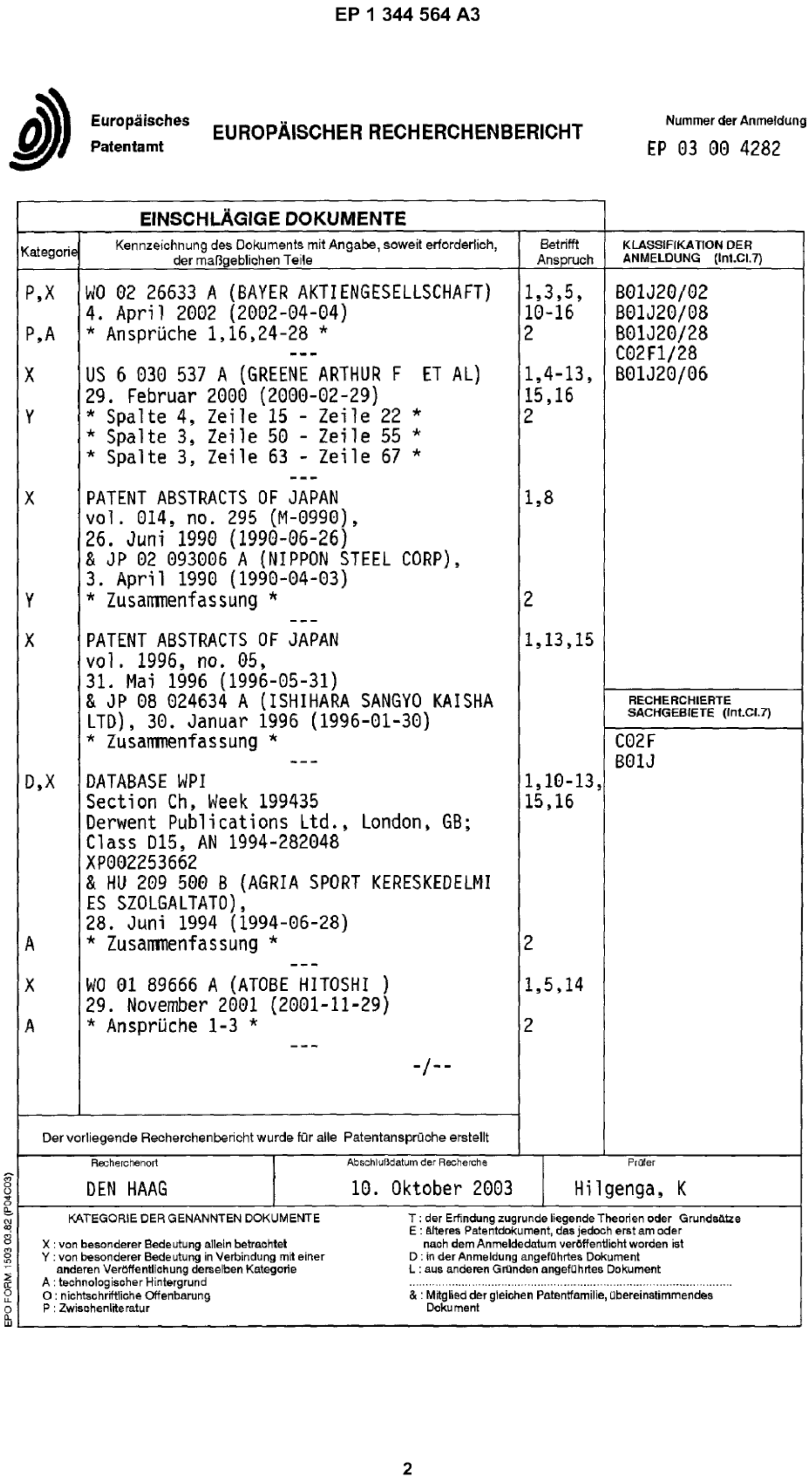

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Europäisches Patentamt

EUROPÄISCHER RECHERCHENBERICHT

Nummer der Anmeldung
EP 03 00 4282

EINSCHLÄGIGE DOKUMENTE

Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betrifft Anspruch	KLASSIFIKATION DER ANMELDUNG (Int.Cl.7)
P,X	WO 02 26633 A (BAYER AKTIENGESELLSCHAFT) 4. April 2002 (2002-04-04)	1,3,5, 10-16	B01J20/02 B01J20/08 B01J20/28 C02F1/28 B01J20/06
P,A	* Ansprüche 1,16,24-28 * ---	2	
X	US 6 030 537 A (GREENE ARTHUR F ET AL) 29. Februar 2000 (2000-02-29)	1,4-13, 15,16	
Y	* Spalte 4, Zeile 15 - Zeile 22 * * Spalte 3, Zeile 50 - Zeile 55 * * Spalte 3, Zeile 63 - Zeile 67 * ---	2	
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 295 (M-0990), 26. Juni 1990 (1990-06-26) & JP 02 093006 A (NIPPON STEEL CORP), 3. April 1990 (1990-04-03)	1,8	
Y	* Zusammenfassung * ---	2	
X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 05, 31. Mai 1996 (1996-05-31) & JP 08 024634 A (ISHIHARA SANGYO KAISHA LTD), 30. Januar 1996 (1996-01-30) * Zusammenfassung * ---	1,13,15	**RECHERCHIERTE SACHGEBIETE (Int.Cl.7)** C02F B01J
D,X	DATABASE WPI Section Ch, Week 199435 Derwent Publications Ltd., London, GB; Class D15, AN 1994-282048 XP002253662 & HU 209 500 B (AGRIA SPORT KERESKEDELMI ES SZOLGALTATO), 28. Juni 1994 (1994-06-28)	1,10-13, 15,16	
A	* Zusammenfassung * ---	2	
X	WO 01 89666 A (ATOBE HITOSHI) 29. November 2001 (2001-11-29)	1,5,14	
A	* Ansprüche 1-3 * --- -/--	2	

Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt

Recherchenort	Abschlußdatum der Recherche	Prüfer
DEN HAAG	10. Oktober 2003	Hilgenga, K

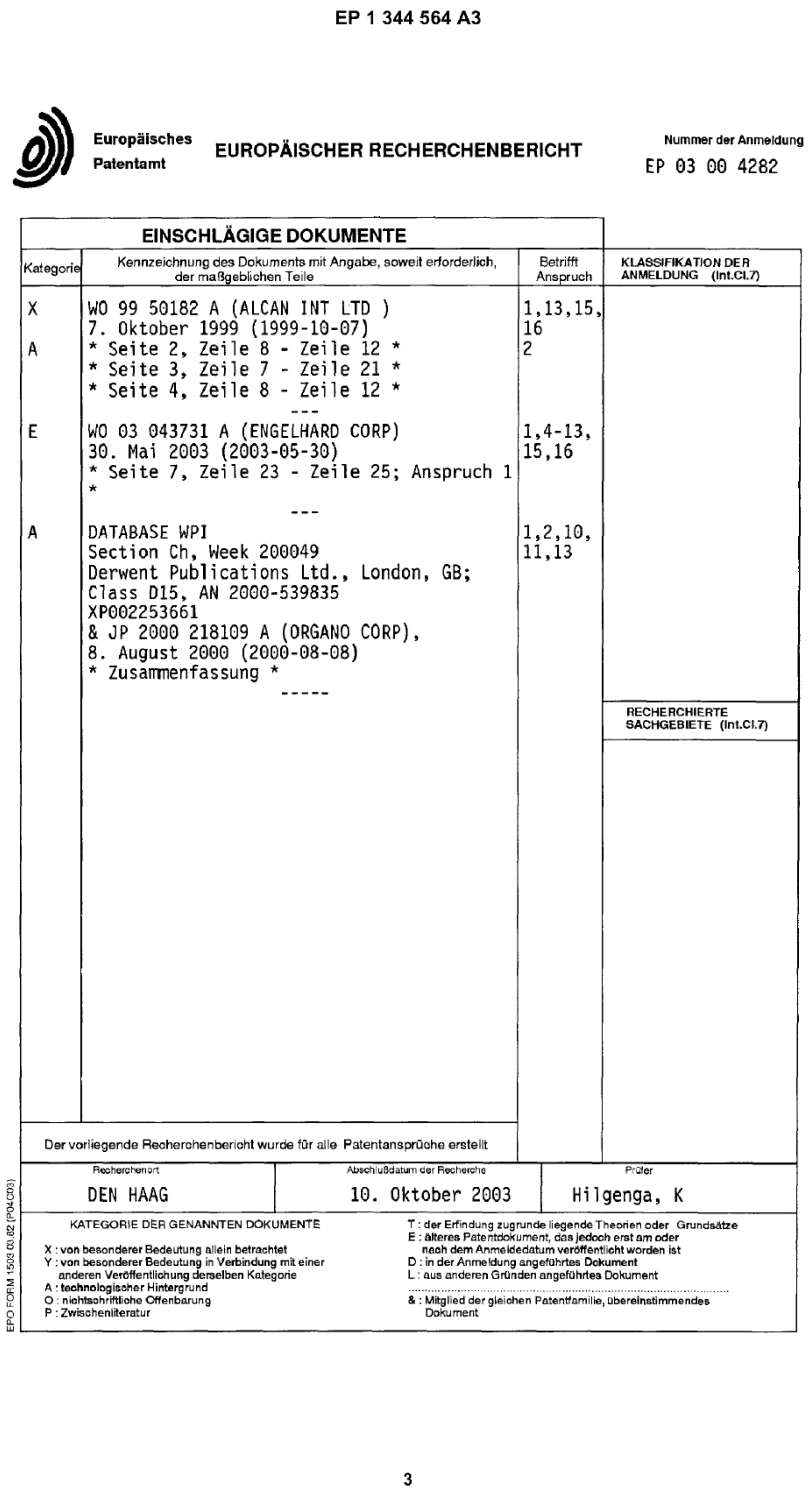
KATEGORIE DER GENANNTEN DOKUMENTE

X : von besonderer Bedeutung allein betrachtet
Y : von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung derselben Kategorie
A : technologischer Hintergrund
O : nichtschriftliche Offenbarung
P : Zwischenliteratur

T : der Erfindung zugrunde liegende Theorien oder Grundsätze
E : älteres Patentdokument, das jedoch erst am oder nach dem Anmeldedatum veröffentlicht worden ist
D : in der Anmeldung angeführtes Dokument
L : aus anderen Gründen angeführtes Dokument

& : Mitglied der gleichen Patentfamilie, übereinstimmendes Dokument

EPO FORM 1503 03.82 (P04C03)



EP 1 344 564 A3

Europäisches Patentamt

EUROPÄISCHER RECHERCHENBERICHT

Nummer der Anmeldung
EP 03 00 4282

EINSCHLÄGIGE DOKUMENTE

Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betrifft Anspruch	KLASSIFIKATION DER ANMELDUNG (Int.Cl.7)
X A	WO 99 50182 A (ALCAN INT LTD) 7. Oktober 1999 (1999-10-07) * Seite 2, Zeile 8 - Zeile 12 * * Seite 3, Zeile 7 - Zeile 21 * * Seite 4, Zeile 8 - Zeile 12 * ---	1,13,15,16 2	
E	WO 03 043731 A (ENGELHARD CORP) 30. Mai 2003 (2003-05-30) * Seite 7, Zeile 23 - Zeile 25; Anspruch 1 * ---	1,4-13,15,16	
A	DATABASE WPI Section Ch, Week 200049 Derwent Publications Ltd., London, GB; Class D15, AN 2000-539835 XP002253661 & JP 2000 218109 A (ORGANO CORP), 8. August 2000 (2000-08-08) * Zusammenfassung * -----	1,2,10,11,13	
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Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt

Recherchenort	Abschlußdatum der Recherche	Prüfer
DEN HAAG	10. Oktober 2003	Hilgenga, K

KATEGORIE DER GENANNTEN DOKUMENTE

X : von besonderer Bedeutung allein betrachtet
Y : von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung derselben Kategorie
A : technologischer Hintergrund
O : nichtschriftliche Offenbarung
P : Zwischenliteratur

T : der Erfindung zugrunde liegende Theorien oder Grundsätze
E : älteres Patentdokument, das jedoch erst am oder nach dem Anmeldedatum veröffentlicht worden ist
D : in der Anmeldung angeführtes Dokument
L : aus anderen Gründen angeführtes Dokument

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EPO FORM 1503 03.82 (P04C03)

3

ANHANG ZUM EUROPÄISCHEN RECHERCHENBERICHT ÜBER DIE EUROPÄISCHE PATENTANMELDUNG NR.

EP 03 00 4282

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten europäischen Recherchenbericht angeführten Patentdokumente angegeben.
Die Angaben über die Familienmitglieder entsprechen dem Stand der Datei des Europäischen Patentamts am
Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

10-10-2003

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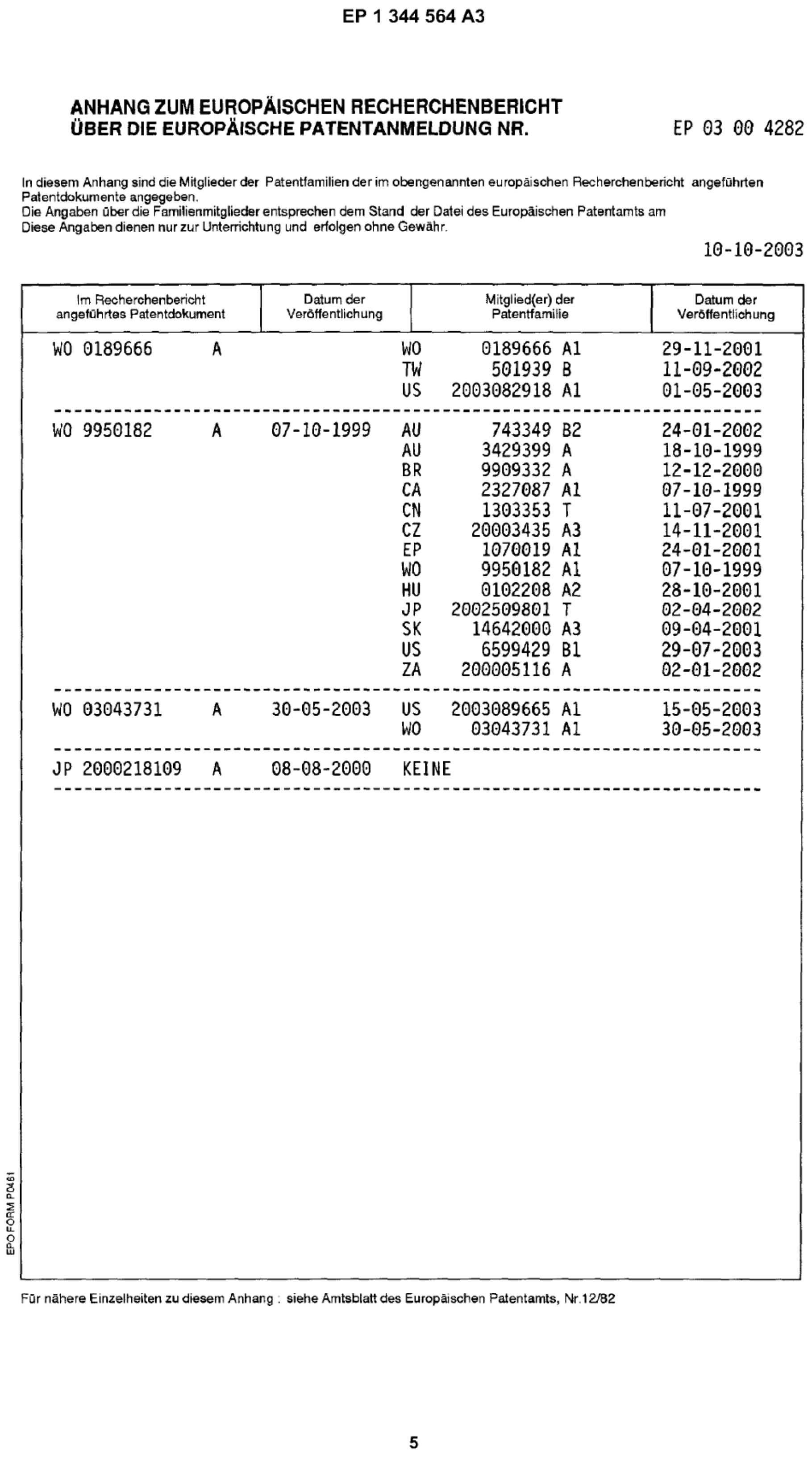
Für nähere Einzelheiten zu diesem Anhang : siehe Amtsblatt des Europäischen Patentamts, Nr.12/82



EP 1 344 564 A3

ANHANG ZUM EUROPÄISCHEN RECHERCHENBERICHT ÜBER DIE EUROPÄISCHE PATENTANMELDUNG NR. EP 03 00 4282

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten europäischen Recherchenbericht angeführten Patentdokumente angegeben.
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Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

10-10-2003

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Für nähere Einzelheiten zu diesem Anhang : siehe Amtsblatt des Europäischen Patentamts, Nr.12/82

5

Rechtstands-Information des Europäischen Patentamts vom 19.05.2015 Seite 1 von 2

EP1344564 - Mischungen aus Adsorbermaterialien

Status	Prüfungsverfahren läuft *Datenbank zuletzt aktualisiert am 18.05.2015*		
Letztes Ereignis	05.03.2015	Neuer Eintrag: Jahresgebühr entrichtet	
Anmelder	Für alle benannten Staaten LANXESS Deutschland GmbH Kennedyplatz 1 50569 Köln / DE [2013/38]		
Erfinder	01 / Schlegel, Andreas, Dr. Bodelschwinghstrasse 12 47800 Krefeld / DE [2003/38]		
Anmeldenummer, Anmeldetag	03004282.4 [2003/38]	27.02.2003	
Prioritätsnummer, Prioritätstag	DE2002110786 [2003/38]	12.03.2002 Ursprünglich veröffentlichtes Format: DE 10210786	
Anmeldesprache	DE		
Verfahrenssprache	DE		
Veröffentlichung	Art:	A2 Anmeldung ohne Recherchenbericht	
	Nr.:	EP1344564	
	Datum:	17.09.2003	
	Sprache:	DE	
	[2003/38]		
	Art:	A3 Recherchenbericht	
	Nr.:	EP1344564	
	Datum:	03.12.2003	
	[2003/49]		
Internationale und ergänzende Recherchenberichte	Ergänzender europäischer Recherchenbericht - versandt am:	EP	22.10.2003
Klassifikation	Internationalen:	B01J20/02, B01J20/08, B01J20/28, C02F1/28, B01J20/06	[2003/49]
Benannte Vertragsstaaten	AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LI, LU, MC, NL, PT, SE, SI, SK, TR [2003/38]		
Bezeichnung der Erfindung	Deutsch:	Mischungen aus Adsorbermaterialien	[2003/38]
	Englisch:	Mixtures of adsorbent materials	[2003/38]
	Französisch:	Mélanges de matériaux adsorbants	[2003/38]
Prüfungsverfahren	03.06.2004	Prüfungsantrag gestellt [2004/32]	
	15.02.2008	Absendung einer Mitteilung der Prüfungsabteilung (Frist: M04)	
	05.06.2008	Erwiderung auf eine Mitteilung der Prüfungsabteilung	
	19.09.2012	Absendung einer Mitteilung der Prüfungsabteilung (Frist: M06)	
	13.05.2013	Absendung der Mitteilung, wonach die Anmeldung als zurückgenommen gilt. Grund: Erwiderung auf die Mitteilung der Prüfungsabteilung nicht fristgerecht eingegangen	

Habbel & Habbel Patentanwälte

Appendix III Composition of Spannenburg and Huijbergen residuals

Parameter	**Huijbergen**	**Spannenburg**
Dry solid, %	14.2	11.4
Al, mg/kg ds	340	120
As, ppm	8	4
Ba, ppm	140	890
Ca, mg/kg ds	29000	74000
P_2O_5, mg/kg ds	38000	25000
Fe, mg/kg ds	440000	310000
Hg ppm	0.25	0.28
Pb ppm	11	<10
Mg, mg/kg ds	460	1300
Mn, mg/kg ds	4300	1800
Organic C, g/kg	40	38
Org.stof %	6.9	6.5
PO_4 mg/kg	32500	49400
PO_4 %	3.25	4.94

Appendix IV Effluent quality of drinking water treatment facility Halsteren

Parameter	Unit	Average concentration
Temperatuur (veldmeting)	˚C	12.3
Zuurstof (labmeting)	mg/l O_2	9.9
Troebeling (veldmeting)	FTE	<0.10
Geleidingsvermogen bij 20˚C (labmeting)	mS/m	33.9
Zuurgraad (veldmeting)	pH	7.78
Totale hardheid	mmol/l	1.54
TOC (Totaal organisch koolstof)	mg/l C	3.3
DOC (Opgelost organisch koolstof)	mg/l C	3.2
Koolstofdioxide	mg/l CO_2	4.5
Waterstofcarbonaat	mg/l HCO_3	177
Carbonaat	mg/l CO_3	<1.0
Fluoride	mg/l F	0.12
Chloride	mg/l Cl	17.5
Sulfaat	mg/l SO_4	24
Silicaat	mg/l SiO_2	24
Ammonium	mg/l NH_4	<0.03
Nitriet	mg/l NO_2	<0.01
Nitraat	mg/l NO_3	2.1
o-Fosfaat	mg/l P	0.008
Totaal fosfaat	mg/l P	0.0046
Natrium	mg/l Na	14
Kalium	mg/l K	2.9
Calcium	mg/l Ca	55
Magnesium	mg/l Mg	4.0
IJzer	mg/l Fe	0.011
Mangaan	mg/l Mn	<0.01
Aluminium	µg/l Al	<5
Arseen	µg/l As	<1
Arseen III	µg/l As	<0.3
Arseen V	µg/l As	0.3
Barium	µg/l Ba	<5
Boor	µg/l B	32
Cadmium	µg/l Cd	<0.1
Chroom	µg/l Cr	<1
Koper	µg/l Cu	<5
Kwik	µg/l Hg	<0.03
Lood	µg/l Pb	<1
Nikkel	µg/l Ni	<1
Seleen	µg/l Se	<1
Zink	µg/l Zn	<5

Appendix V Pictures and scanning electron micrographs

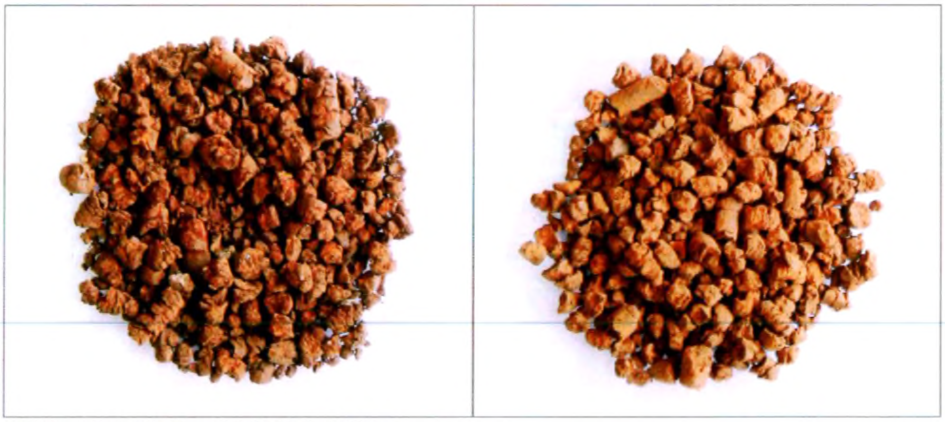


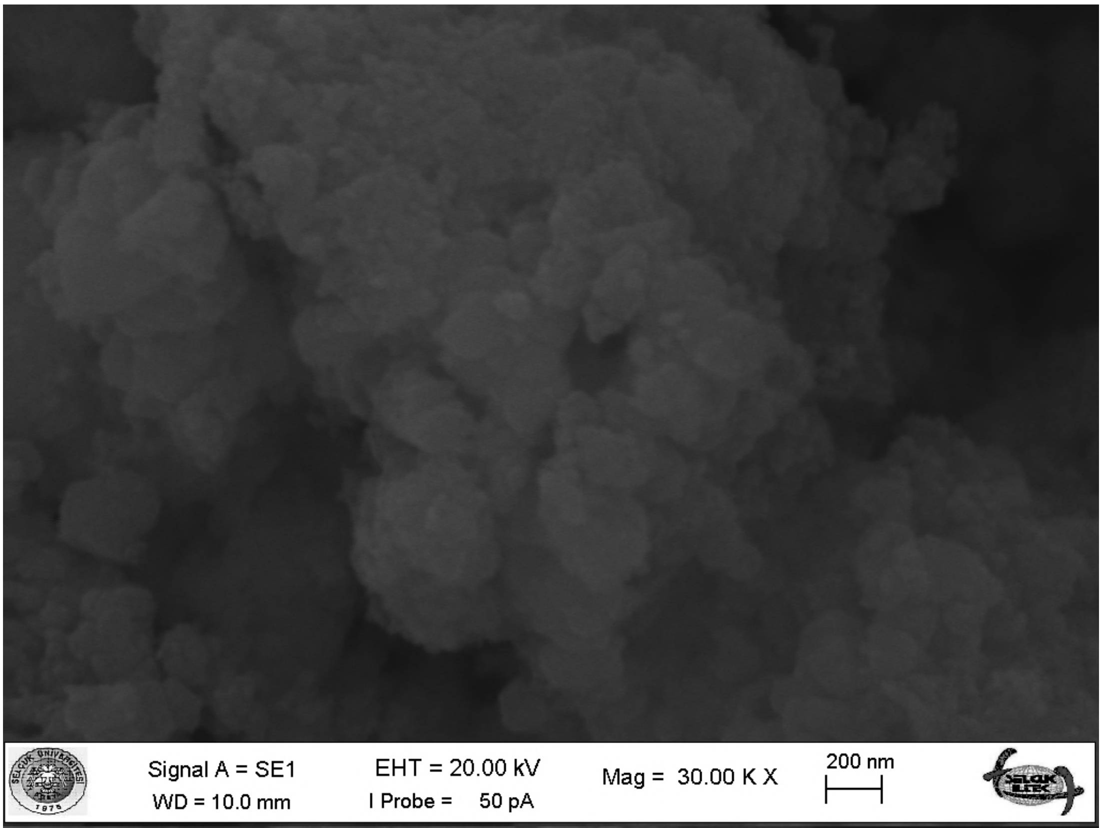
Abbildung 2: 1-GIH (li) und 2-GIH inkl. CMC (re)

Abbildung 3: 3-GIH exkl. CMC (li) und 4-GIH SPA+ (re)

Abbildung 4: 5-GIH SPA OUD (li) und 6-GIH SPA VERS (re)

Abbildung 5: 7-GIH MENG

Huijbergen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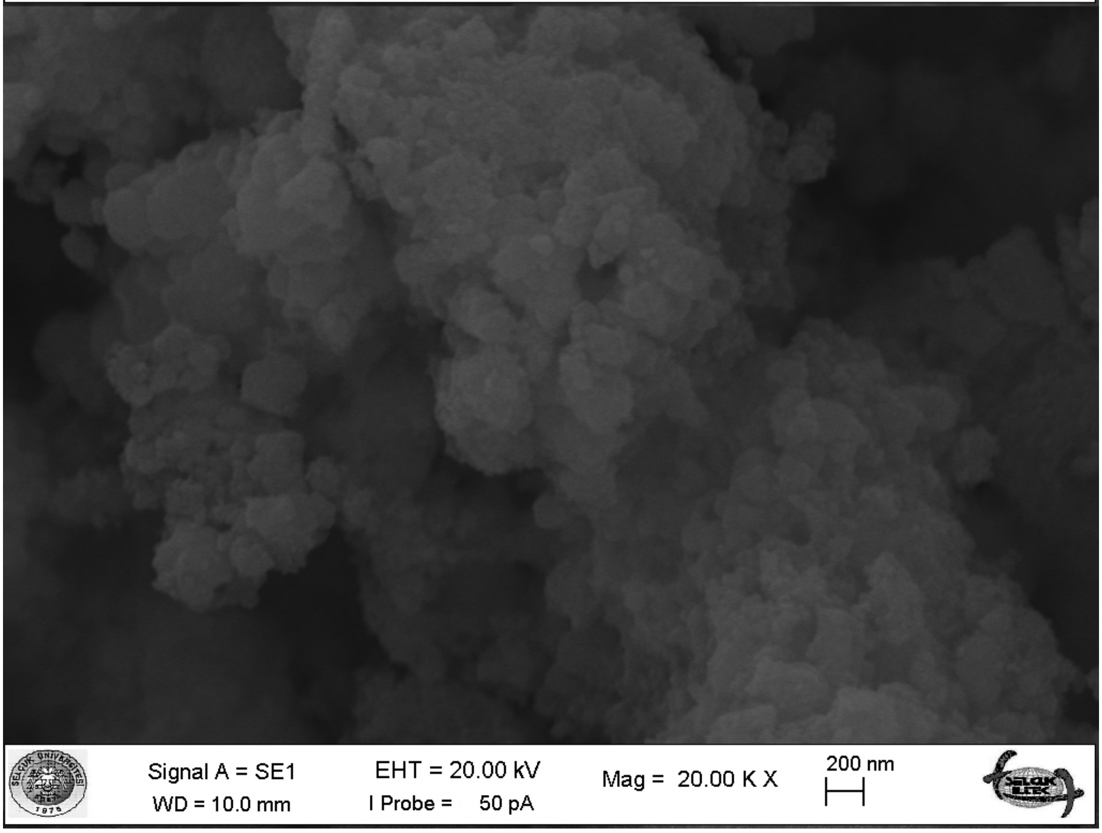
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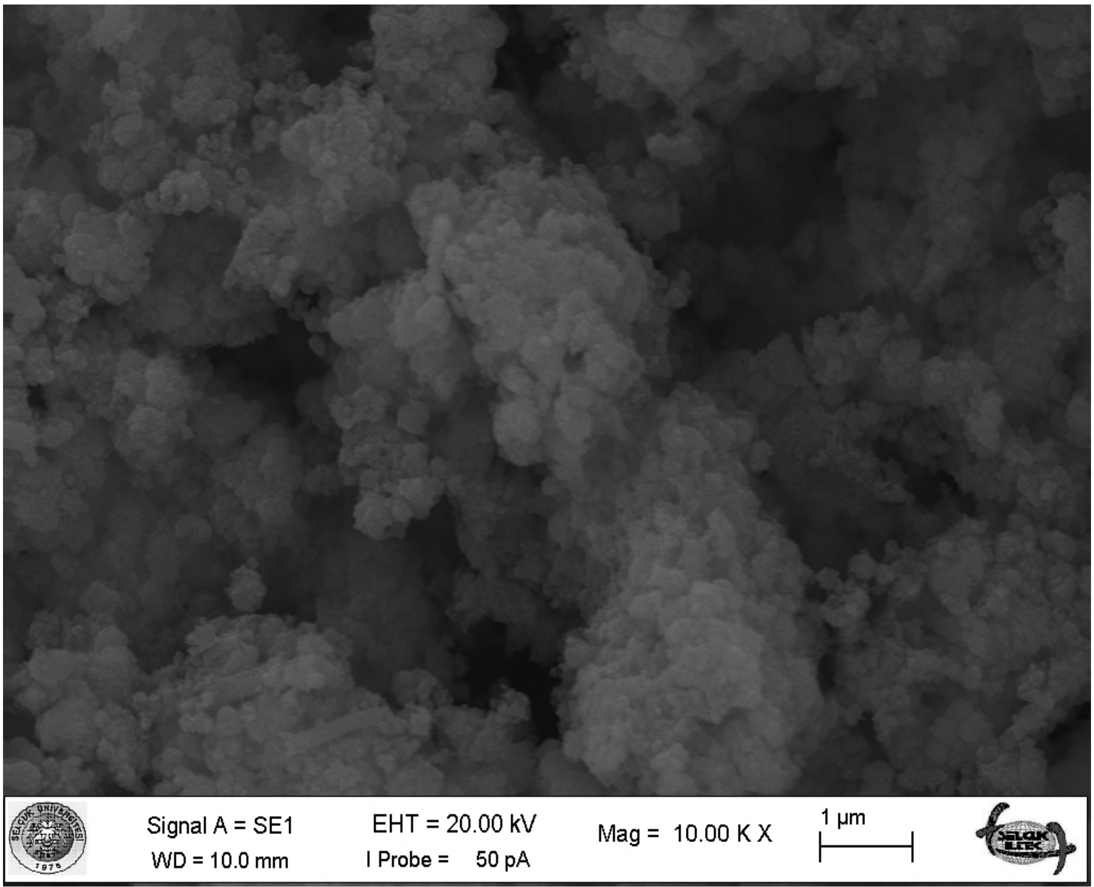
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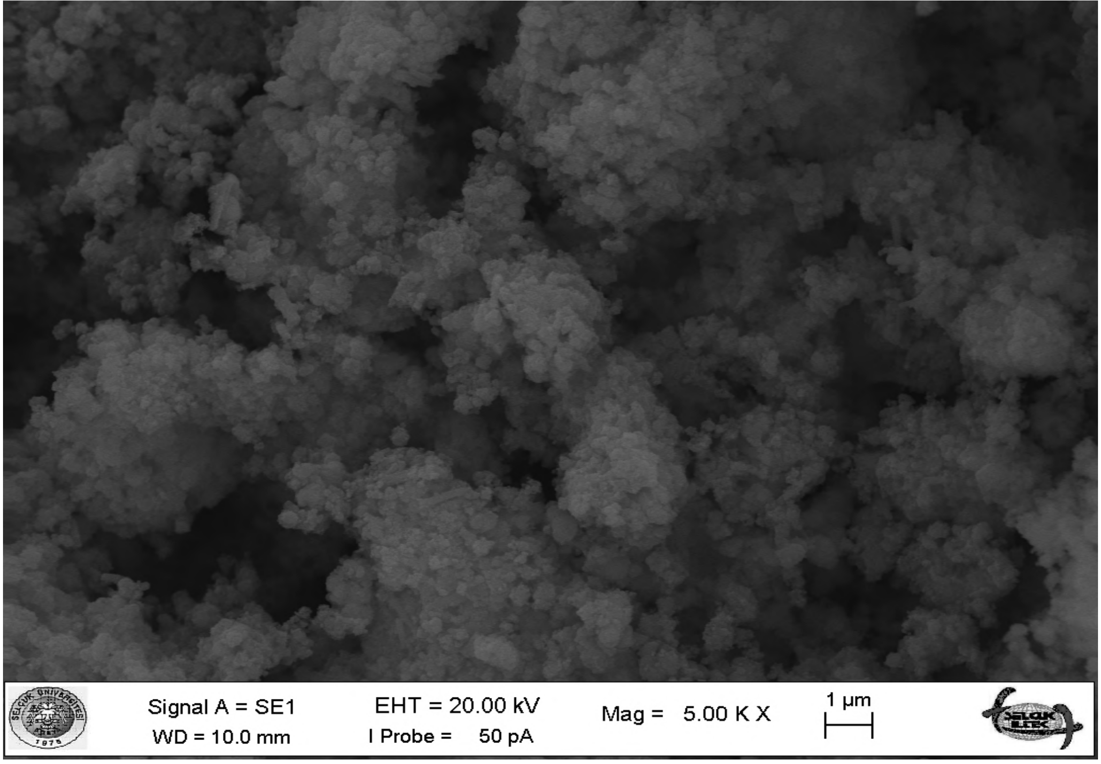
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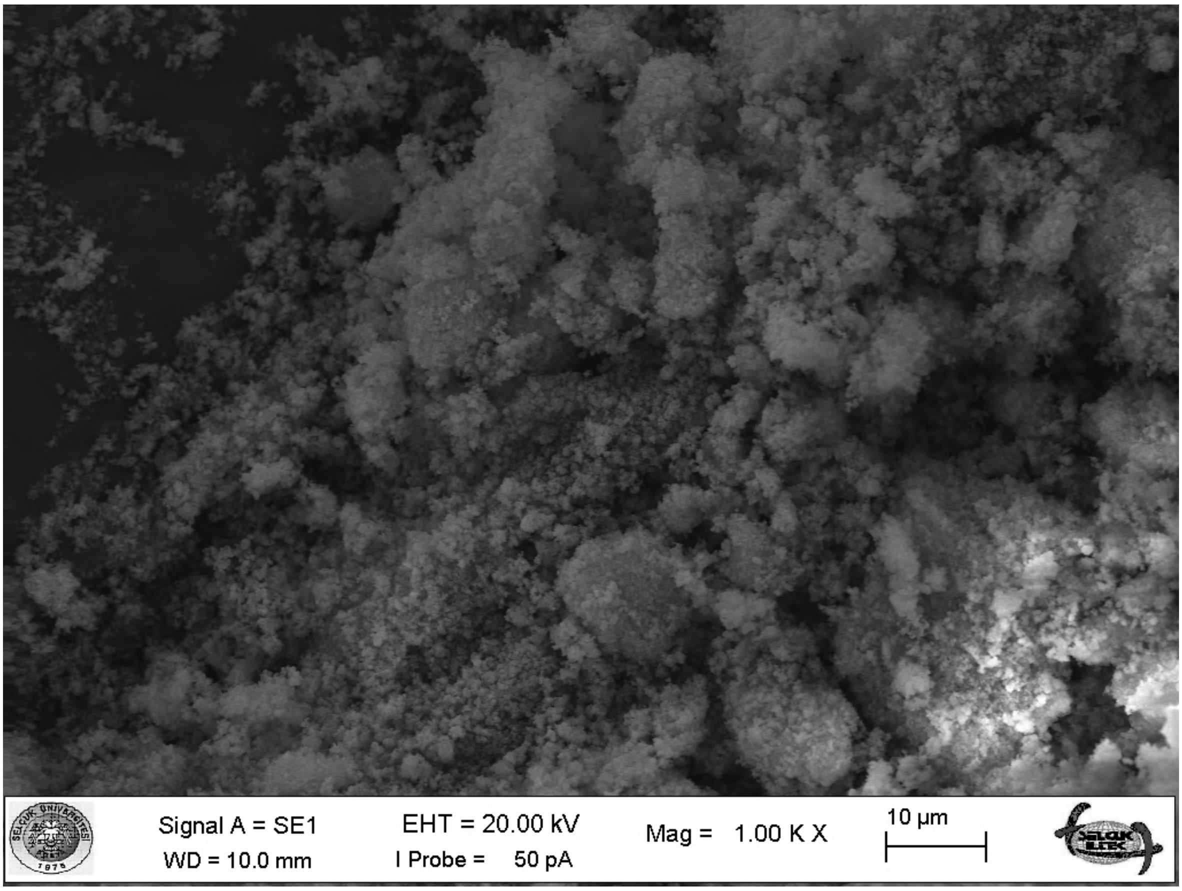
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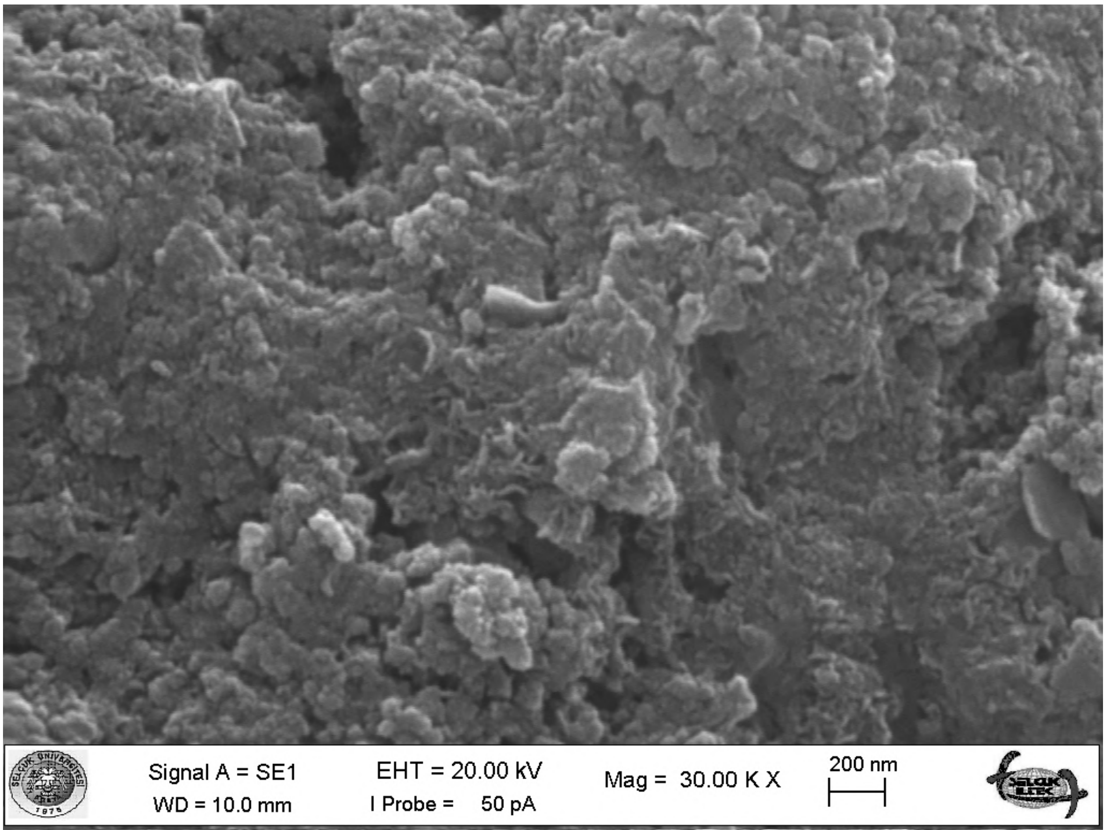
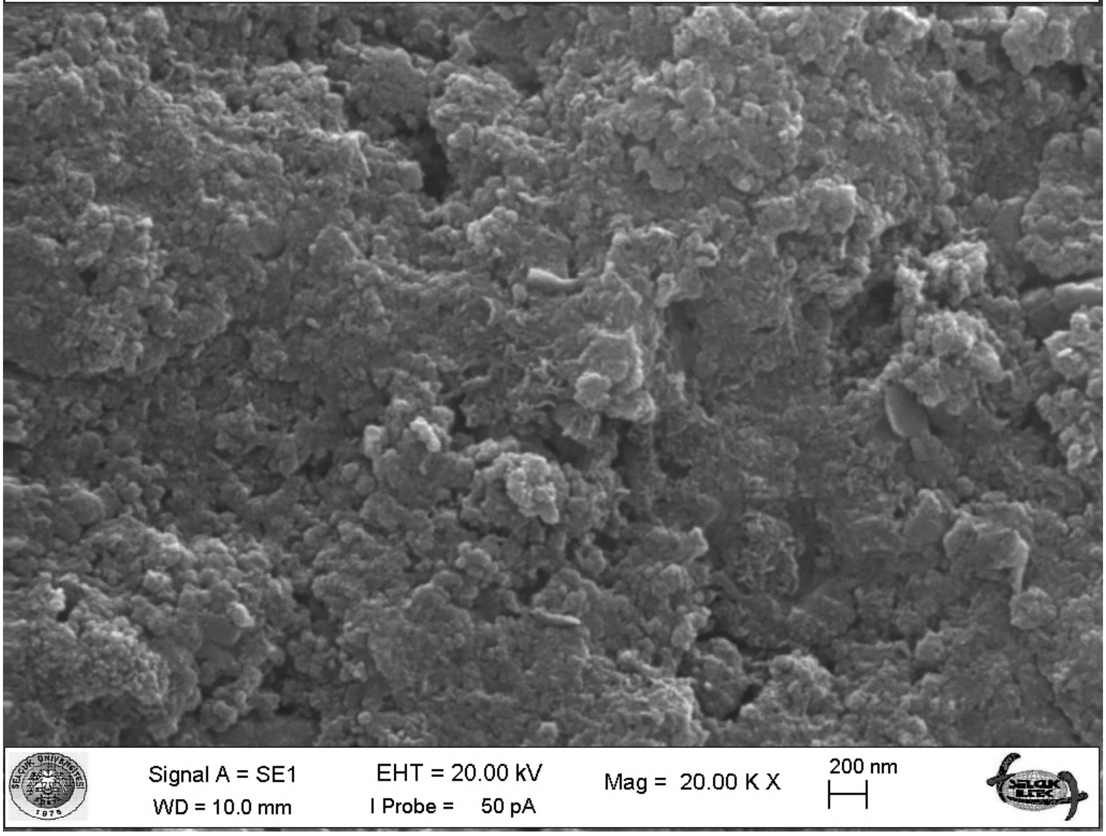
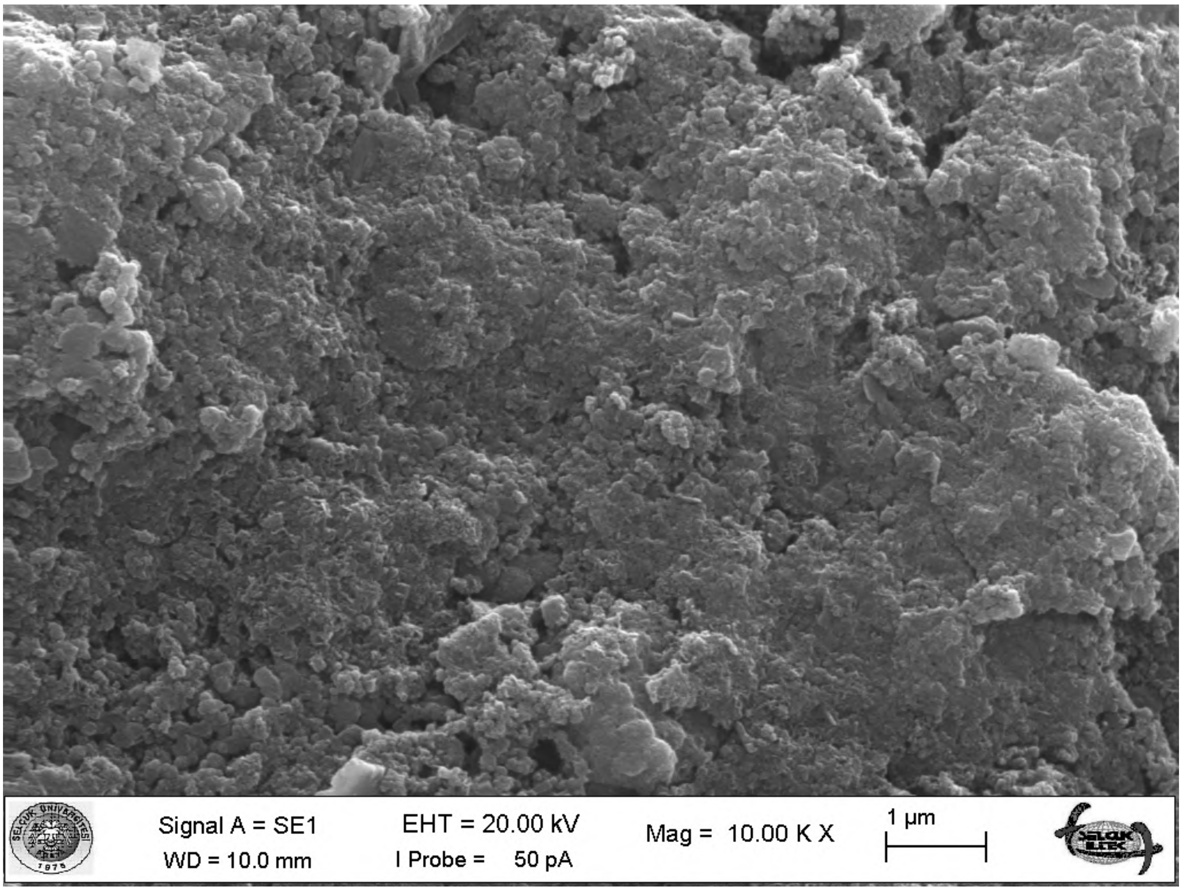
Spannenburg met flocculant



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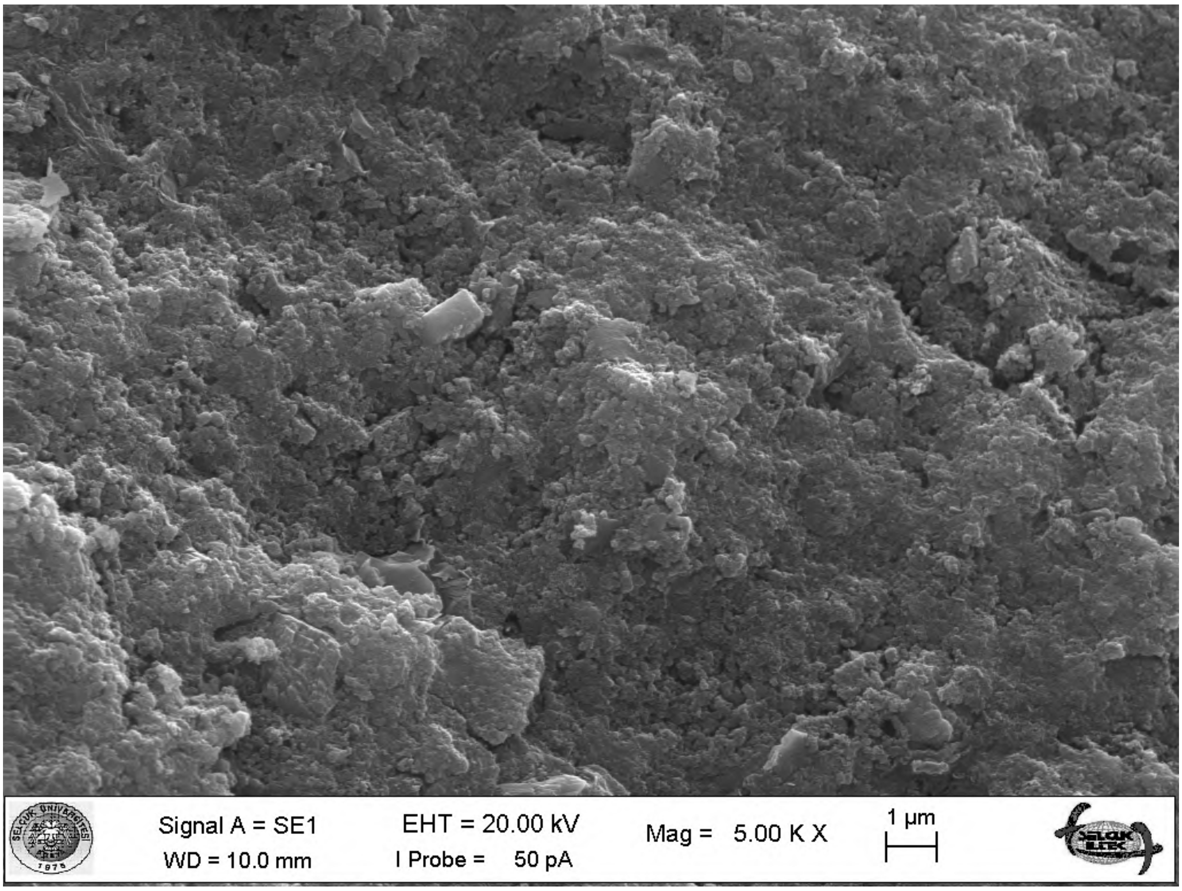
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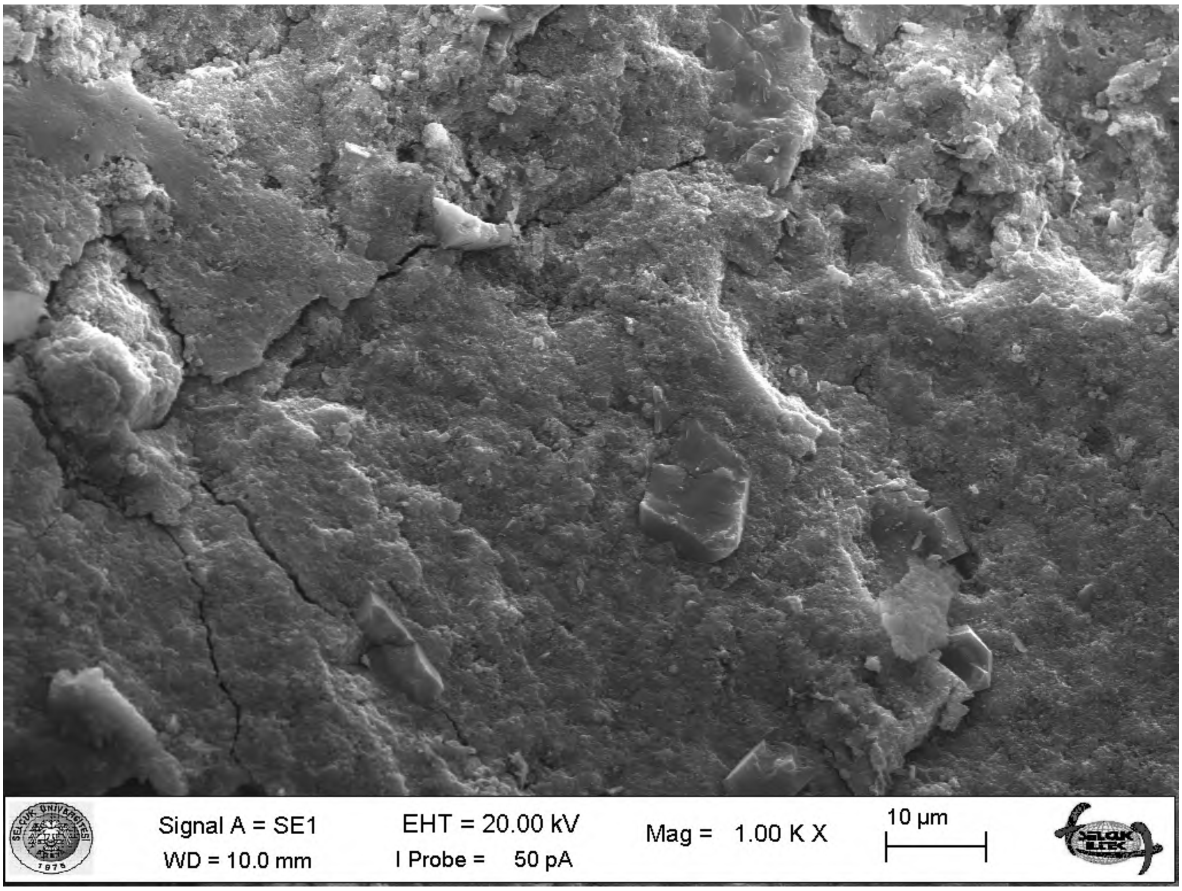
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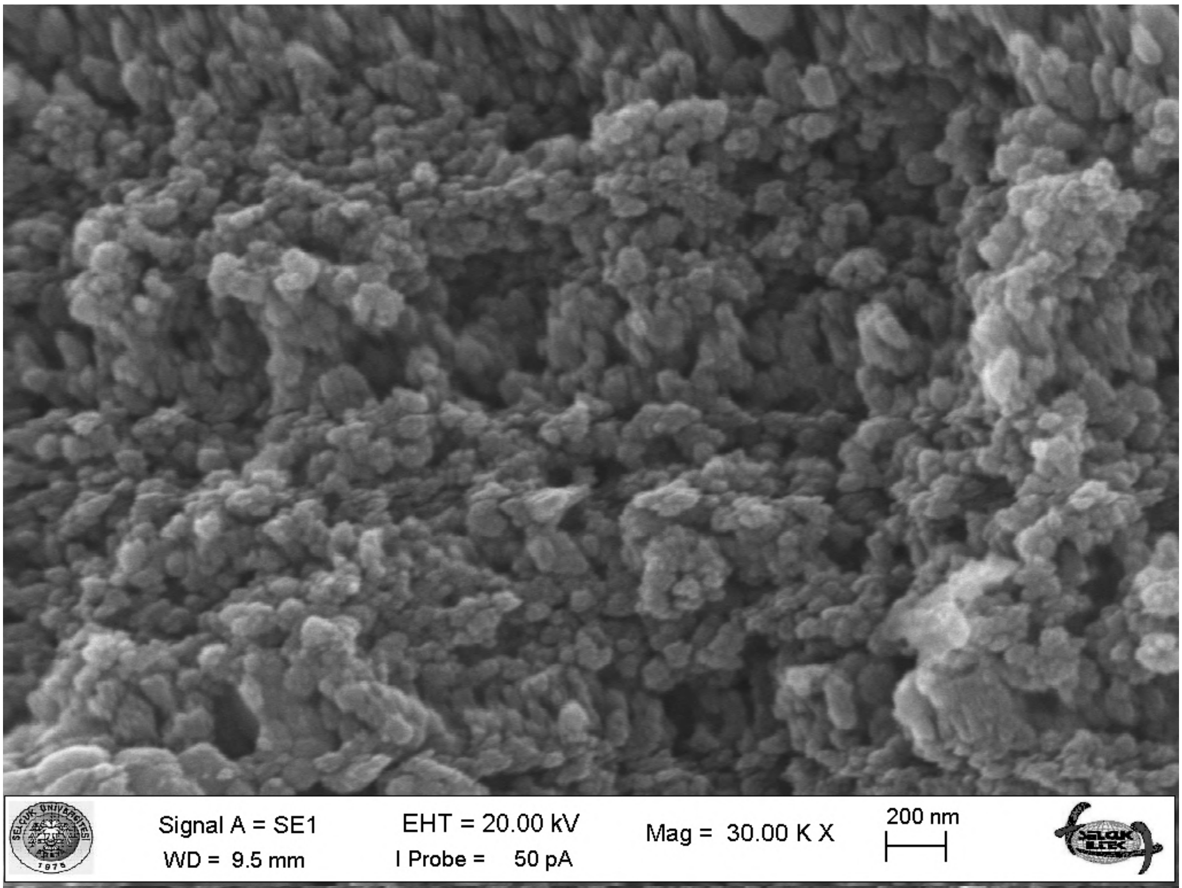
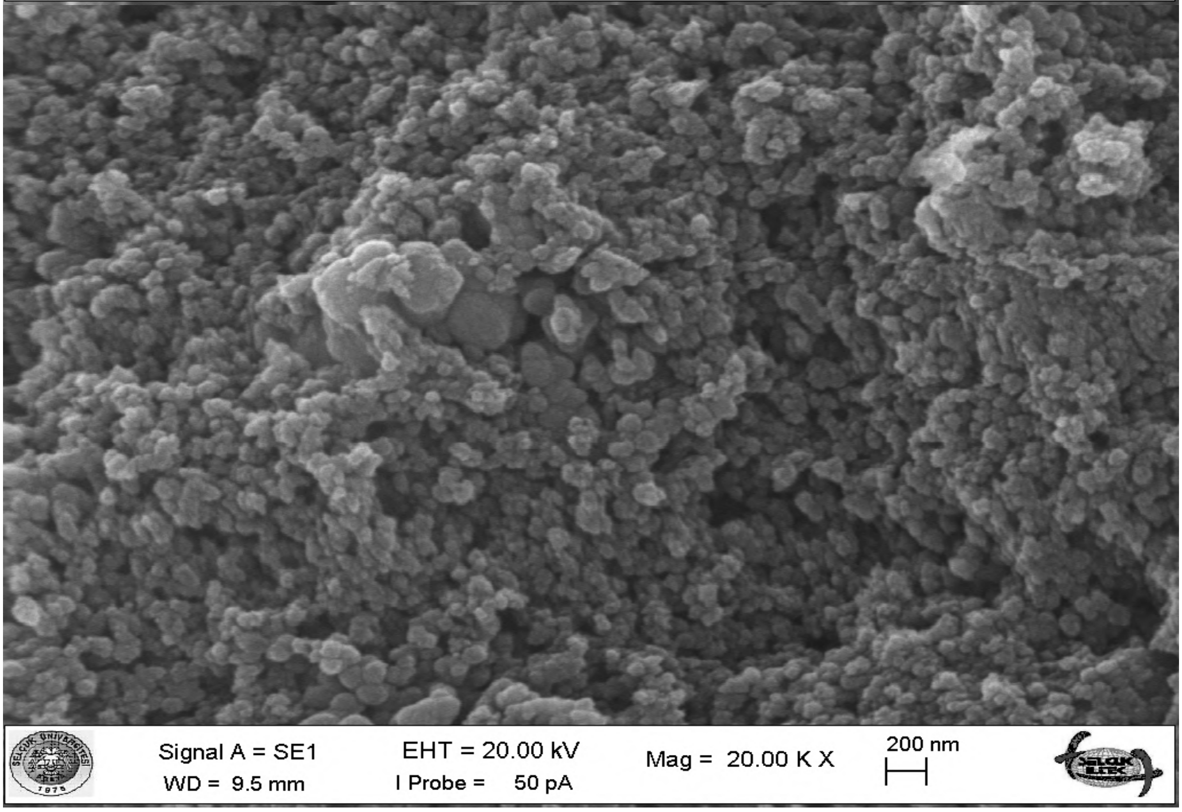
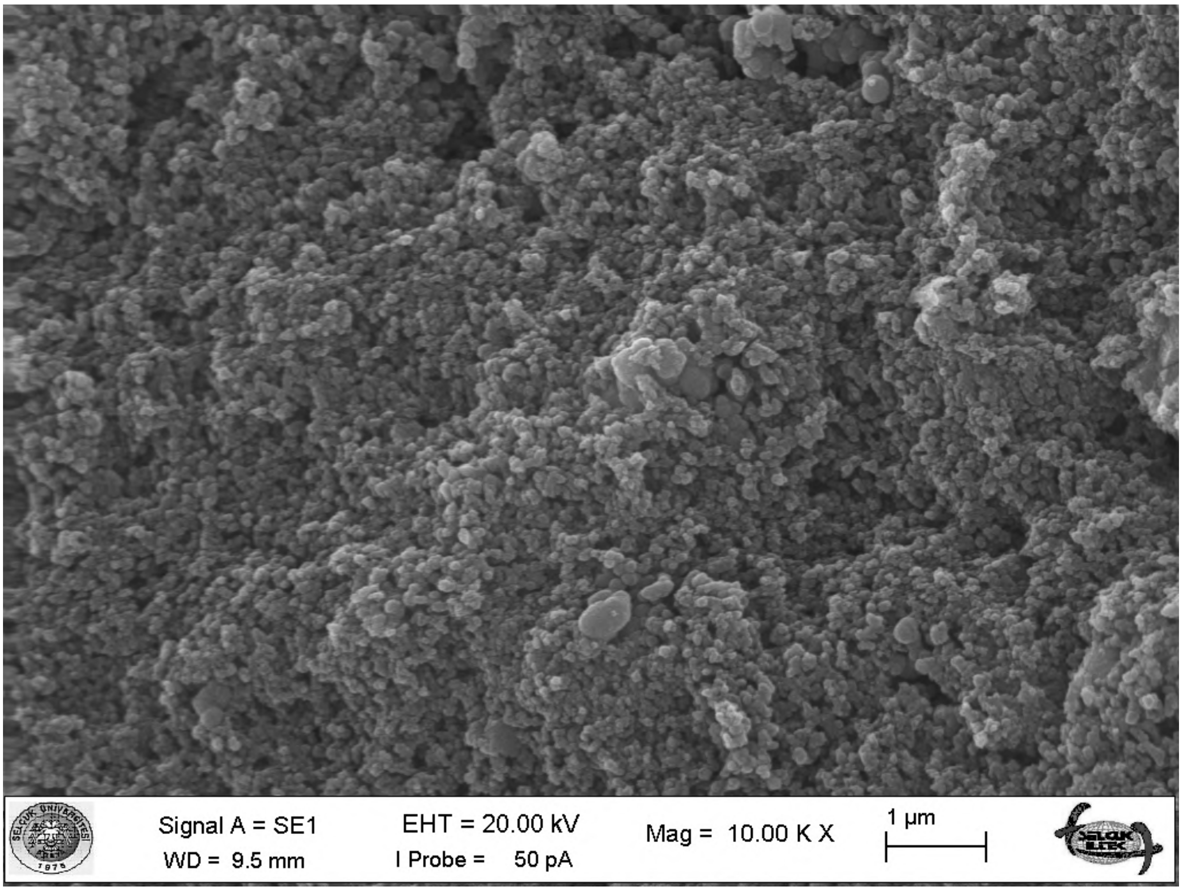
Beladen materiaal:



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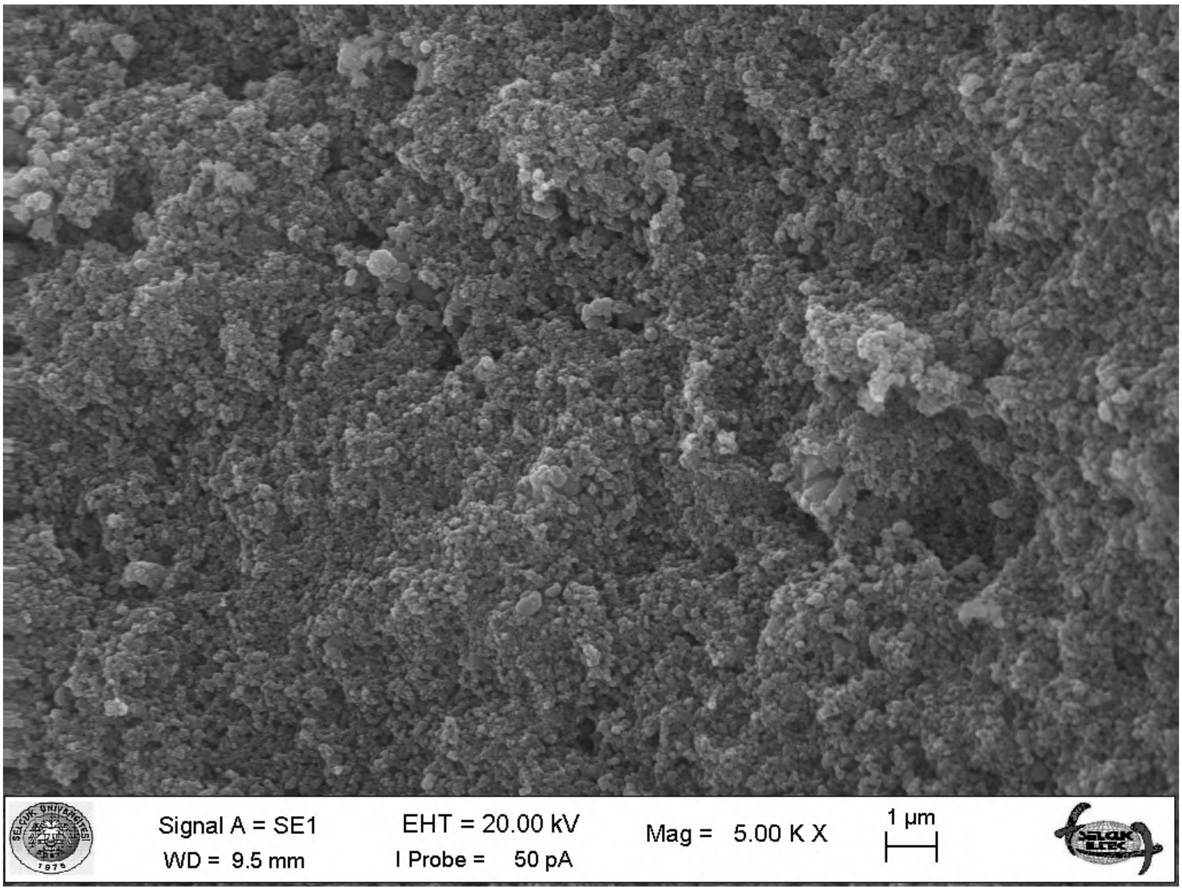
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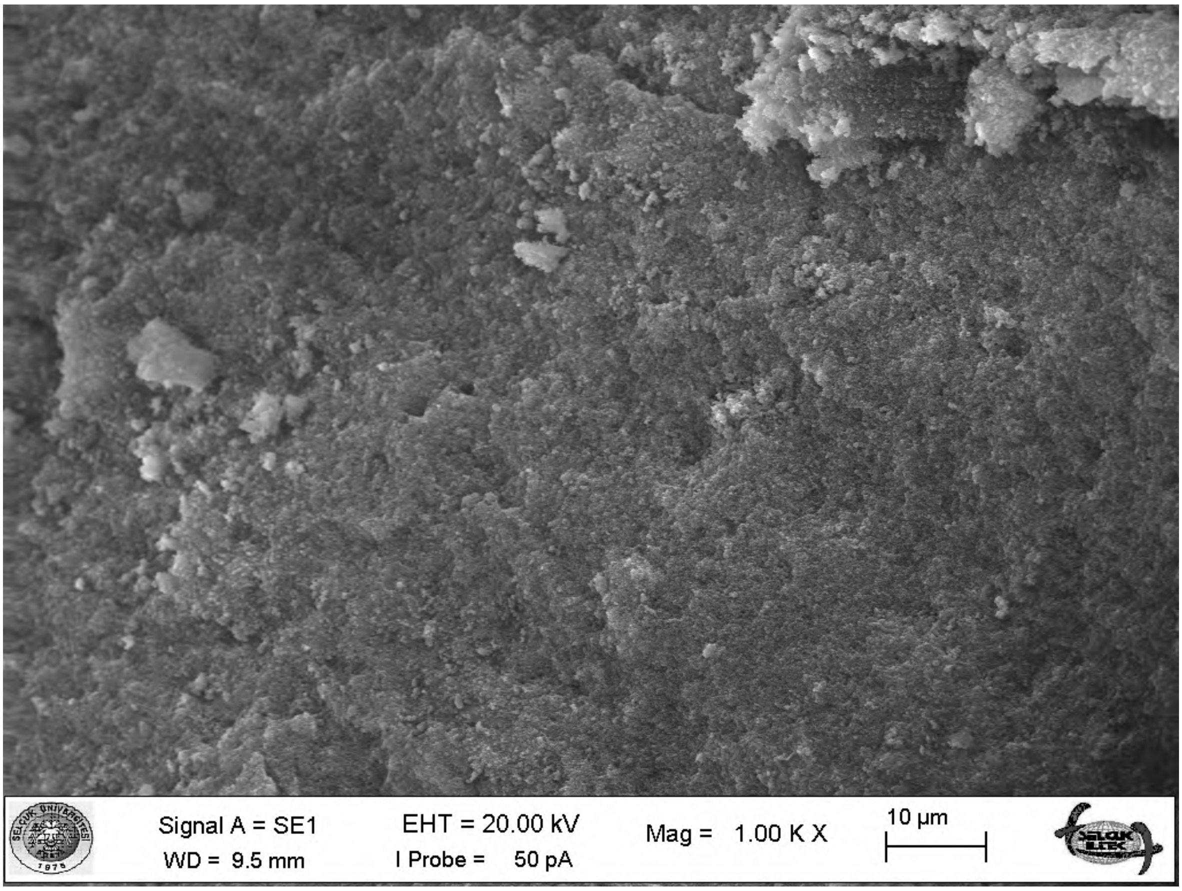
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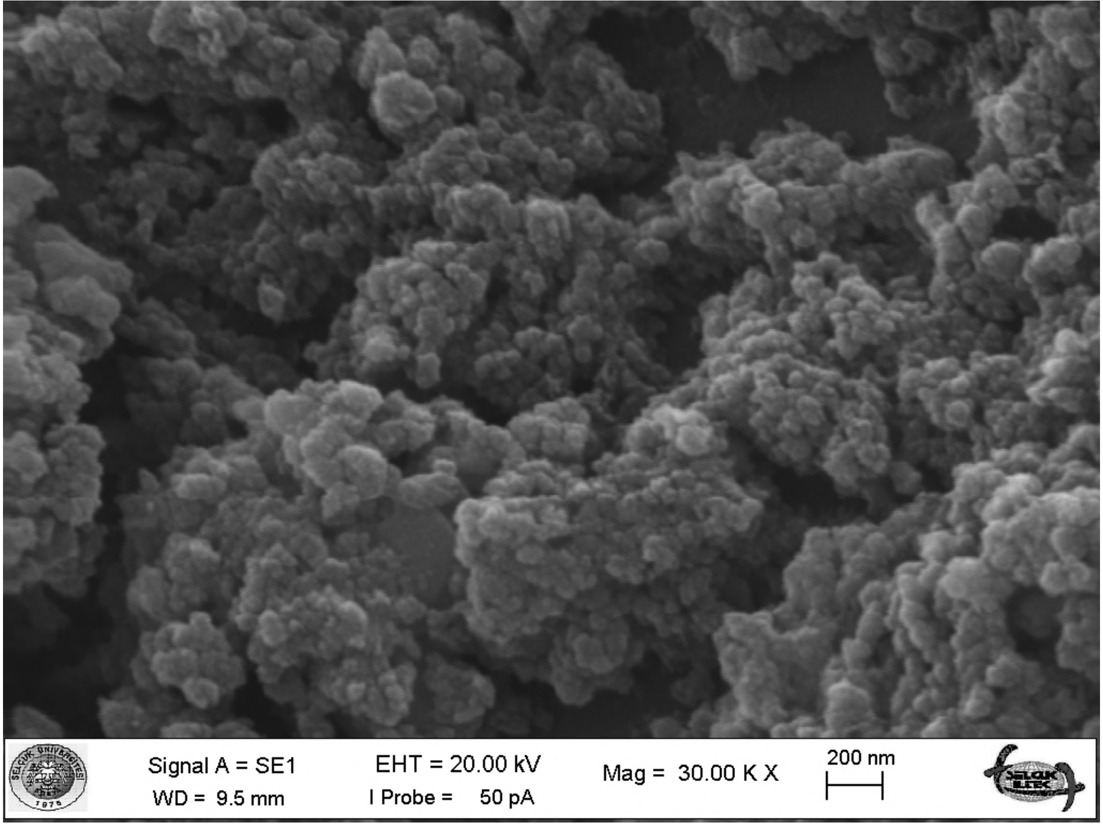
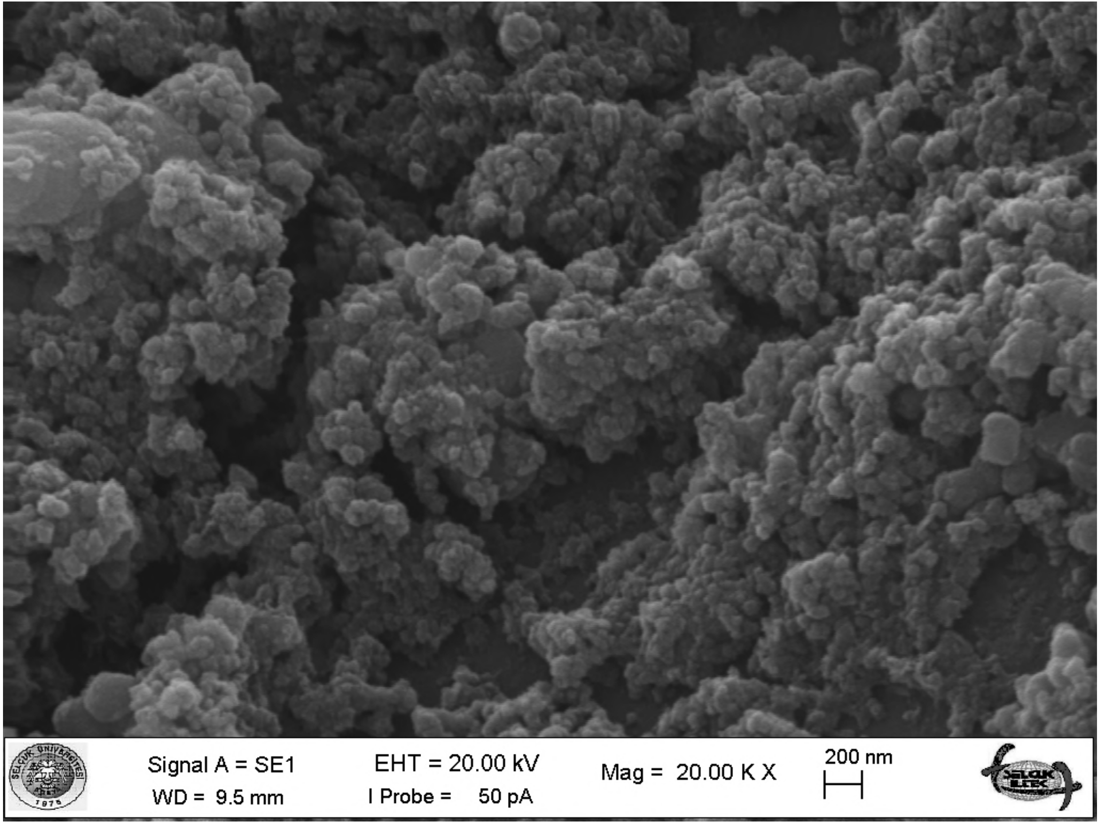
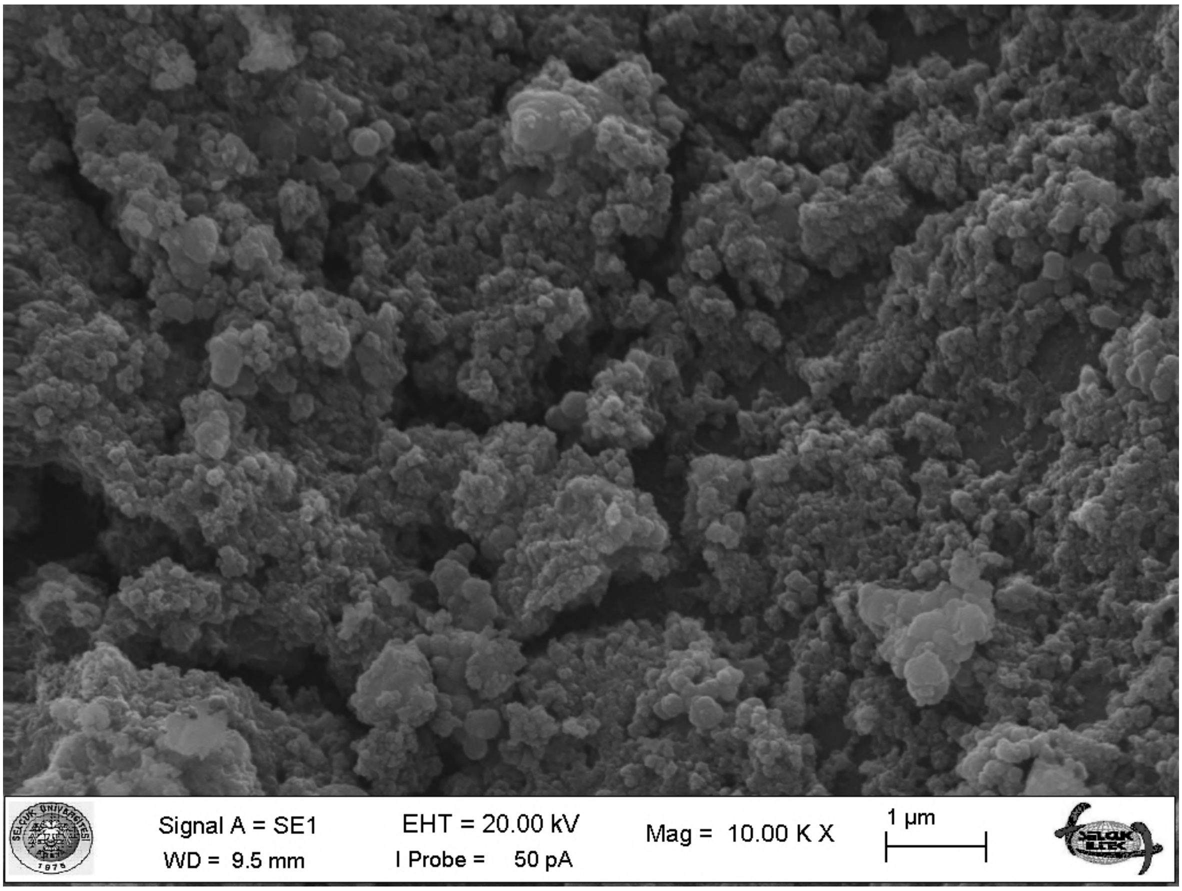
Spannenburg oud 22-1-15



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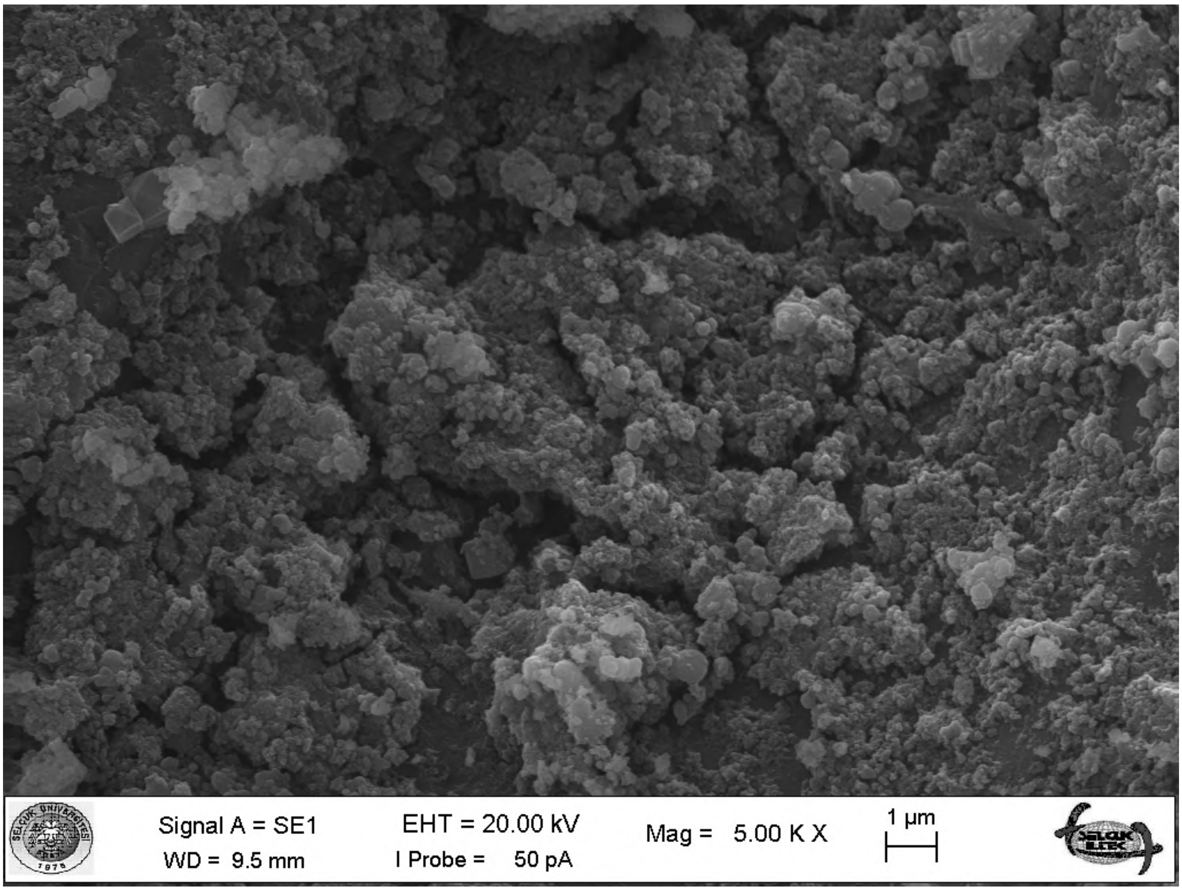
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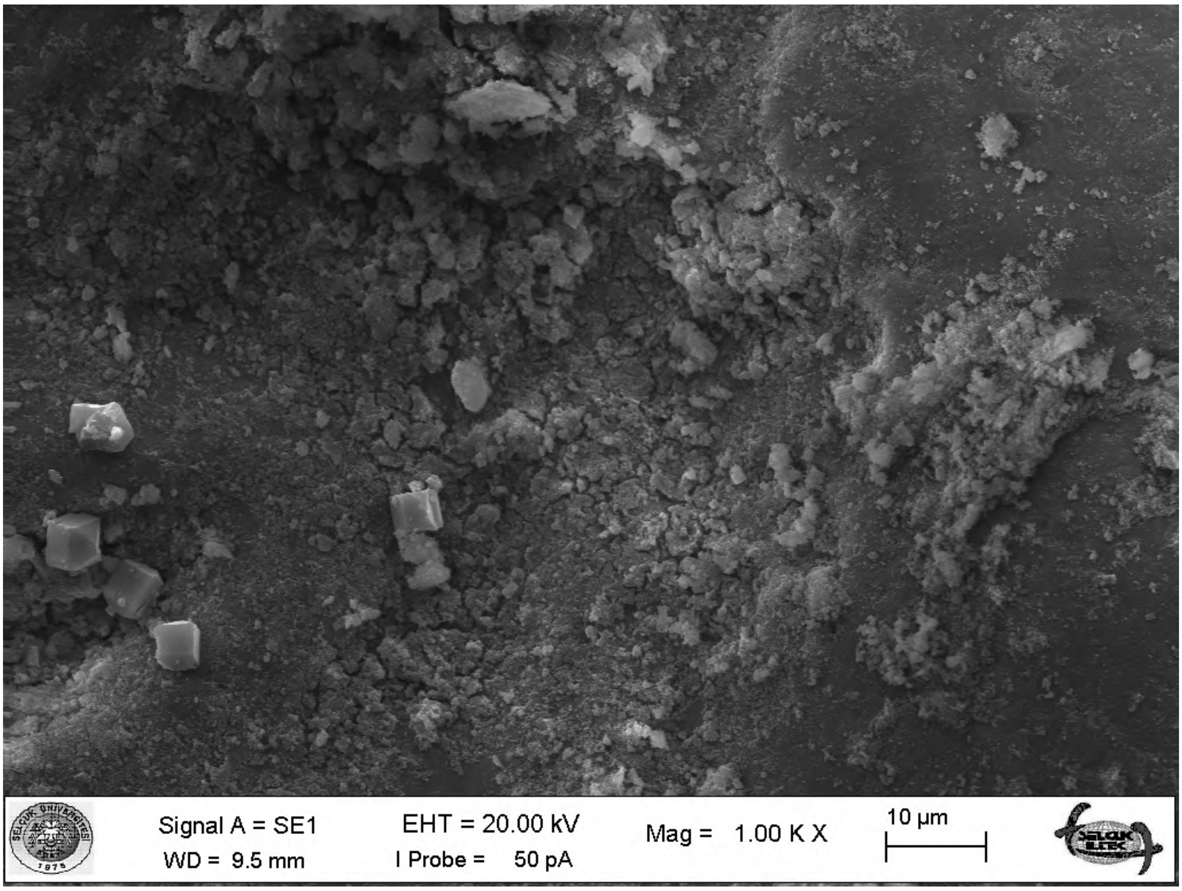
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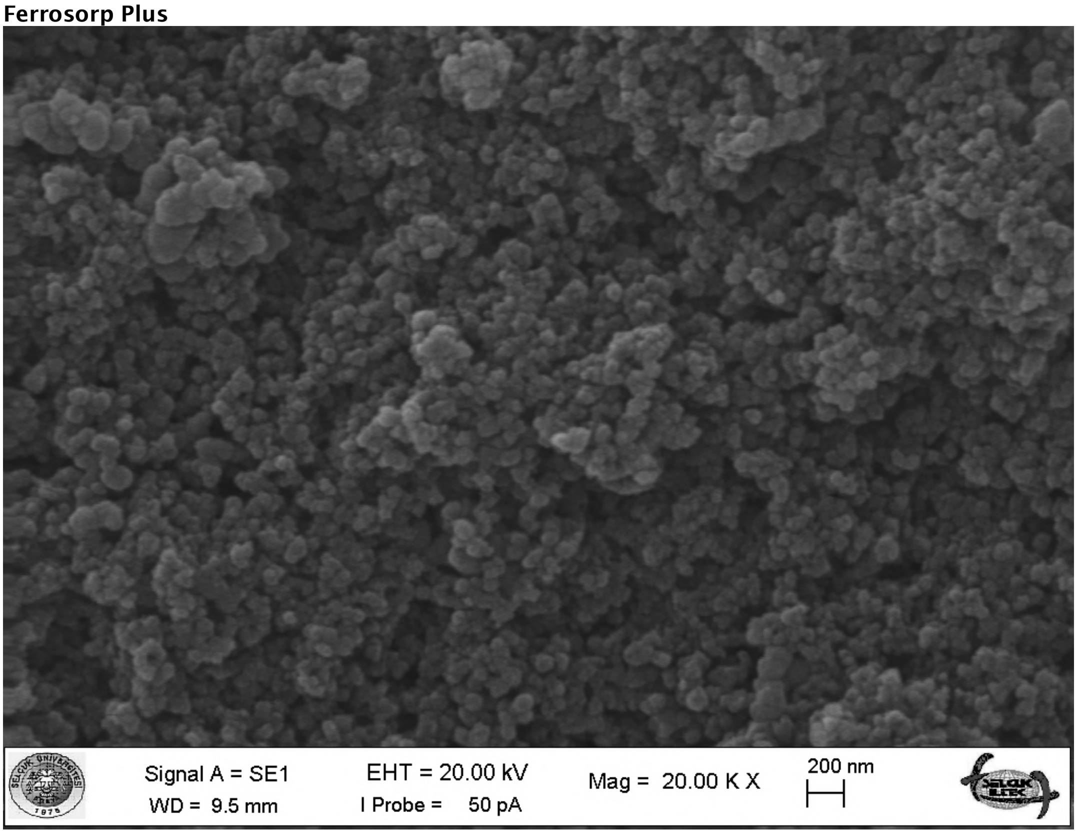
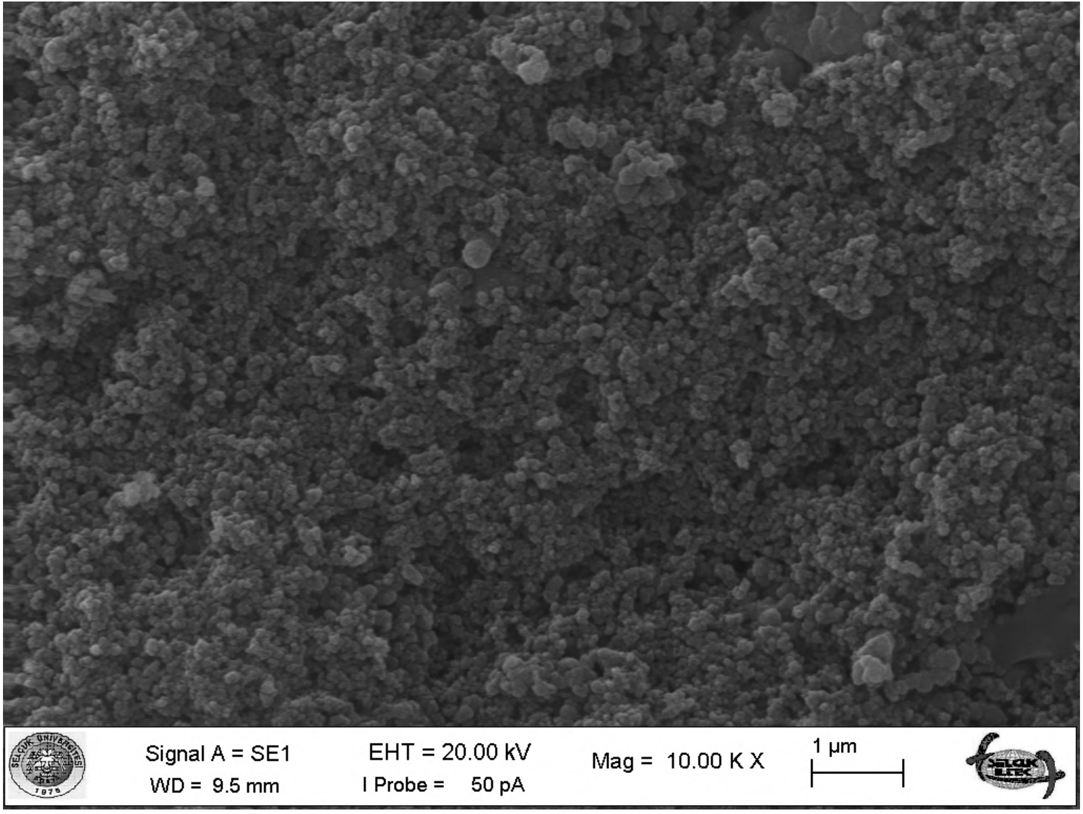
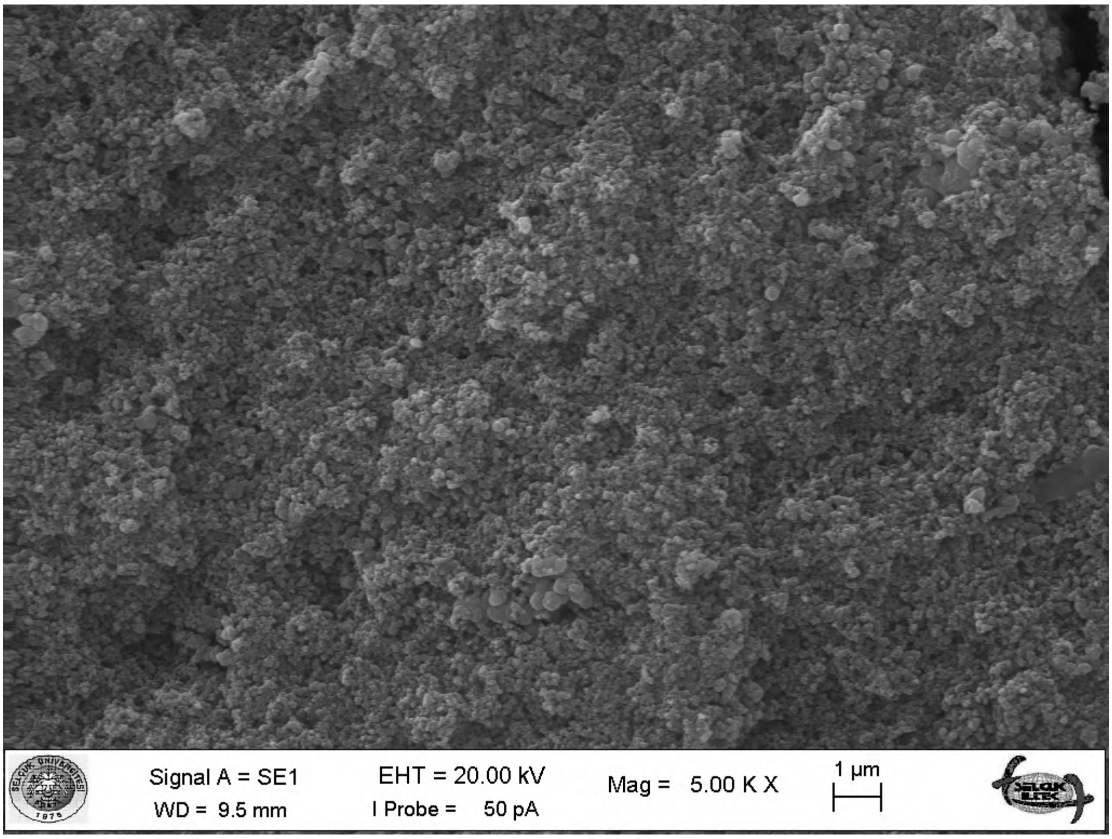
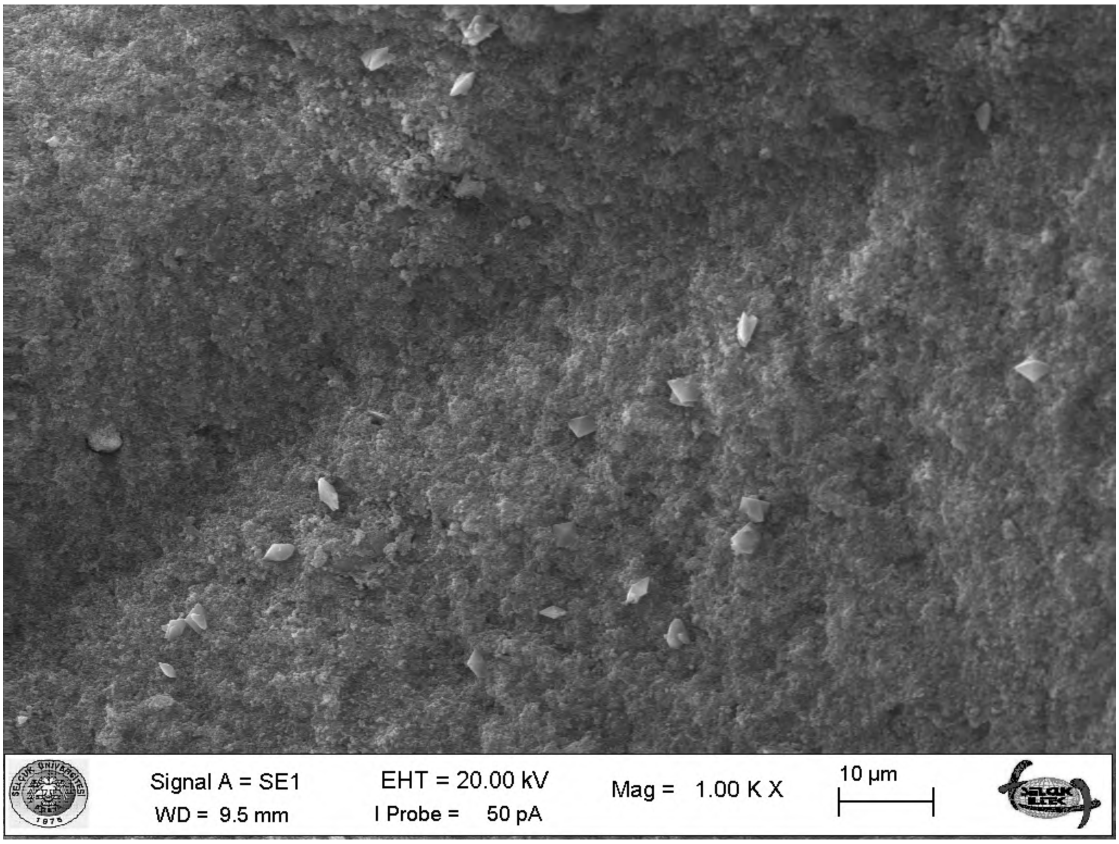
WD = 9.5 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 1.00 K X
10 µm

Ferrosorp Plus

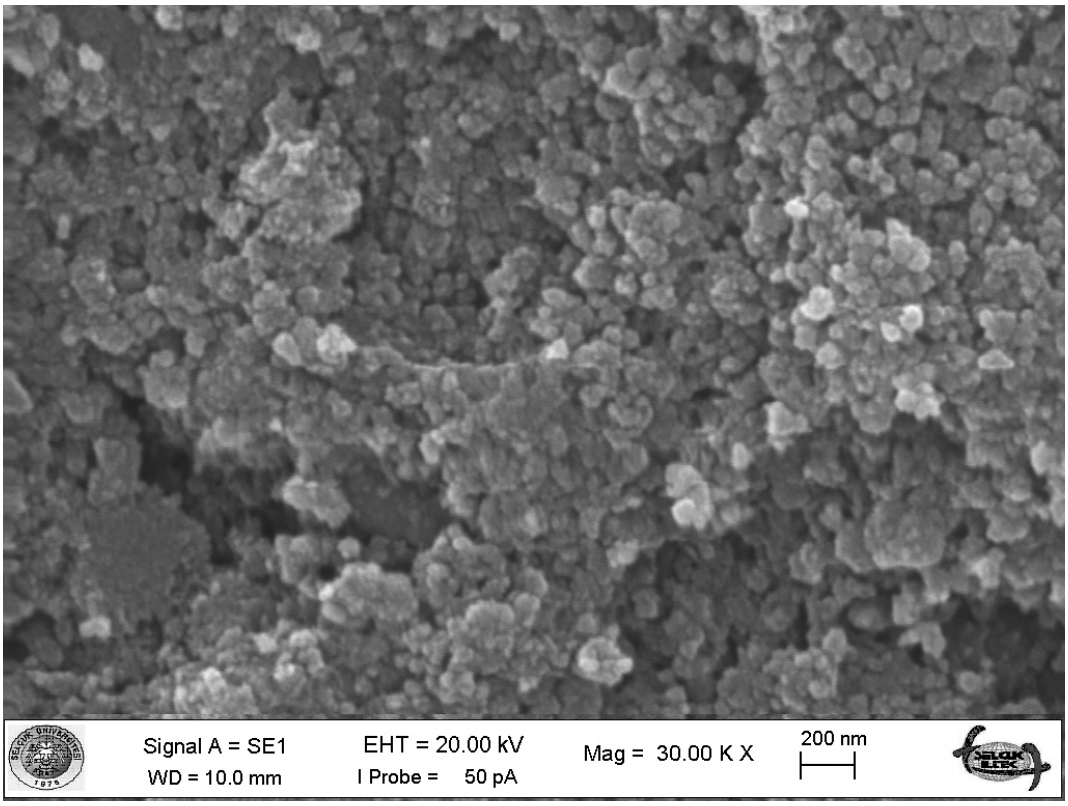


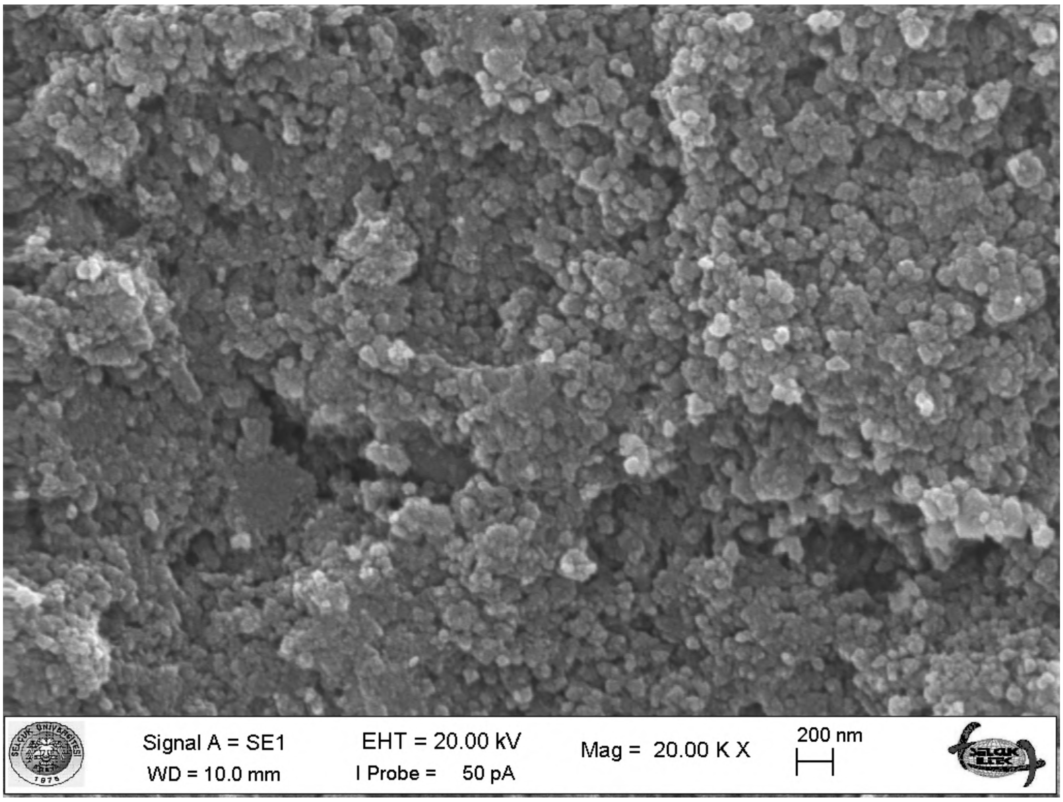


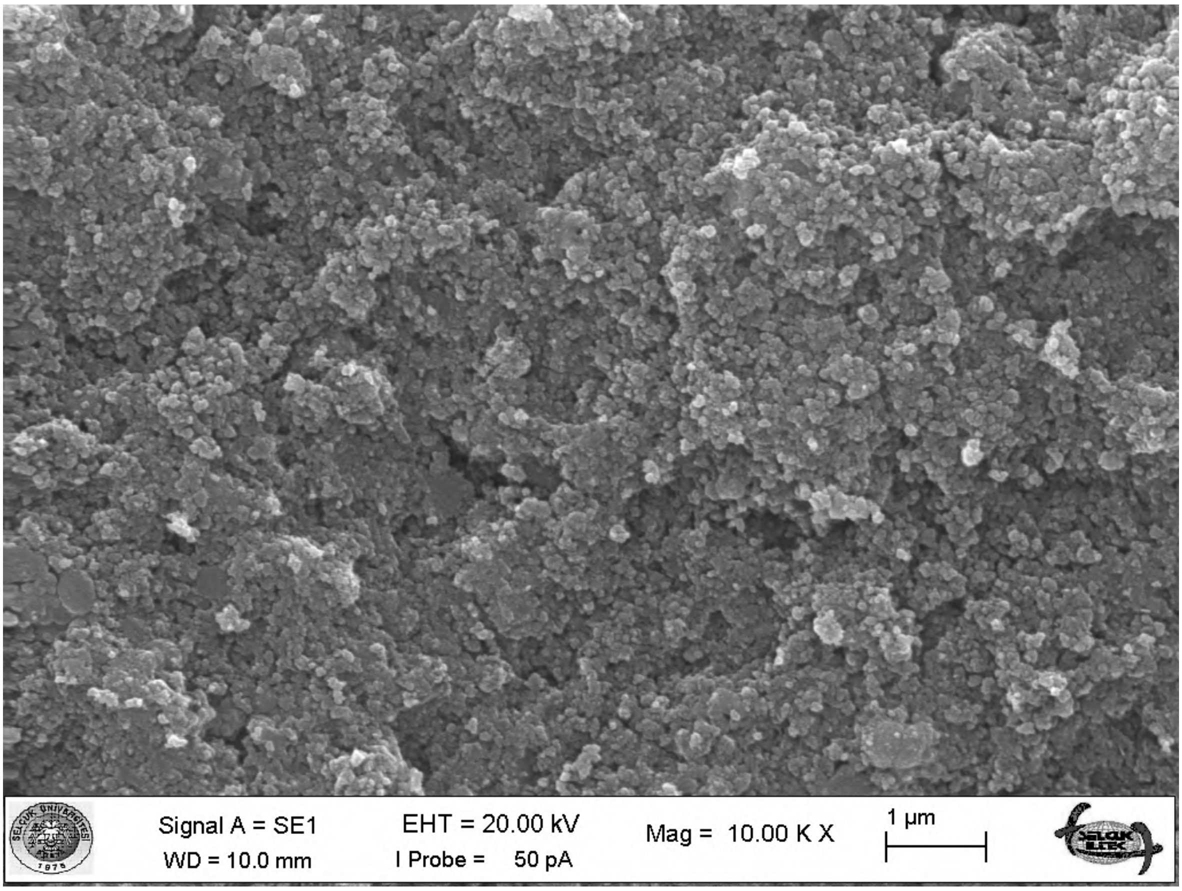

Signal A = SE1
WD = 9.5 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 5.00 K X
1 µm

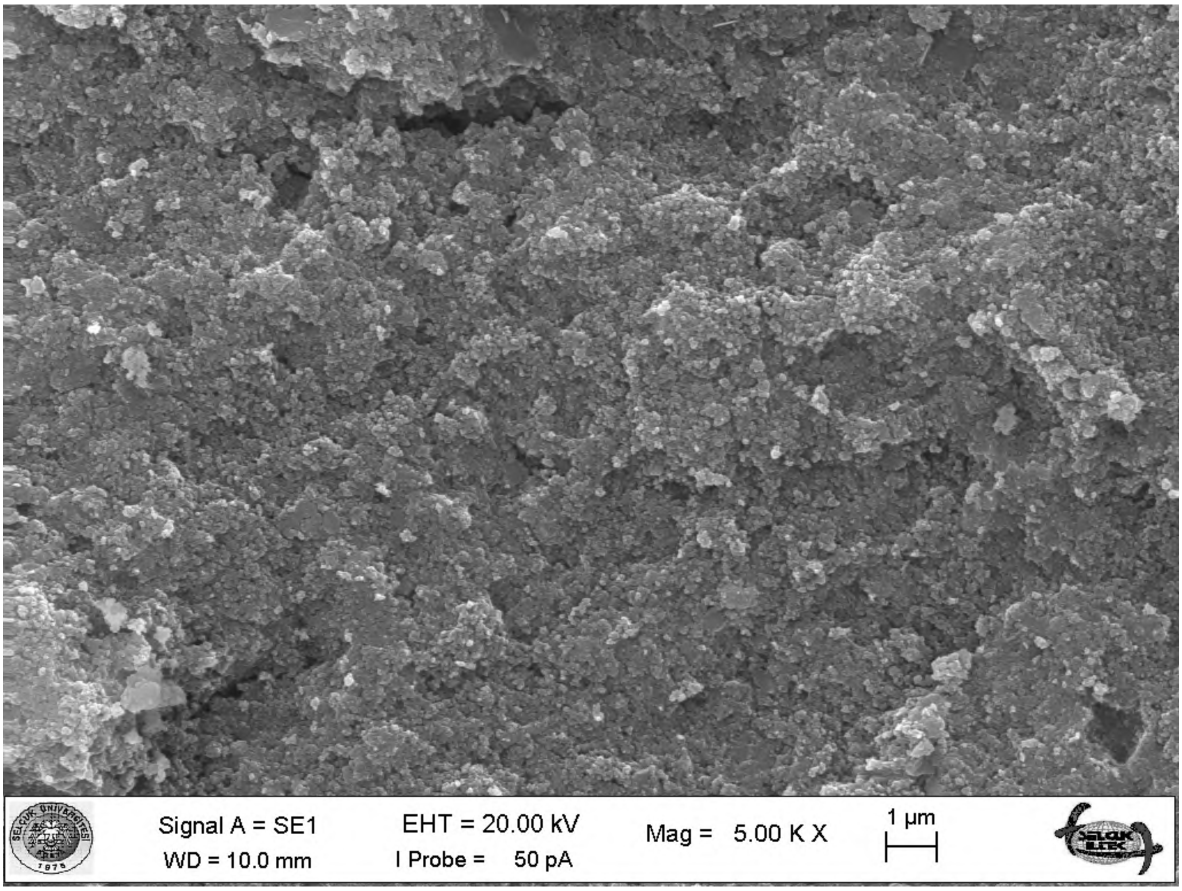

Signal A = SE1
WD = 9.5 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 1.00 K X
10 µm

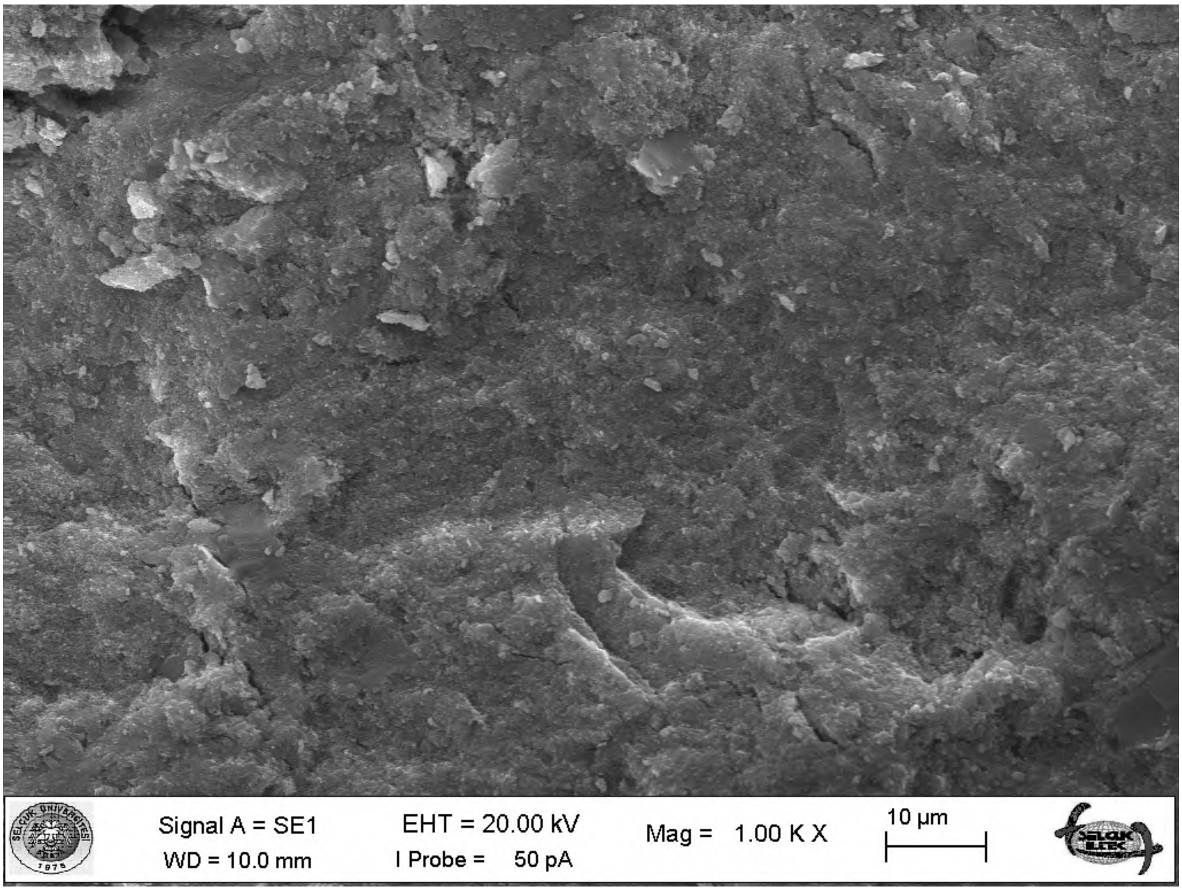
Agravis


Signal A = SE1
WD = 10.0 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 30.00 K X
200 nm

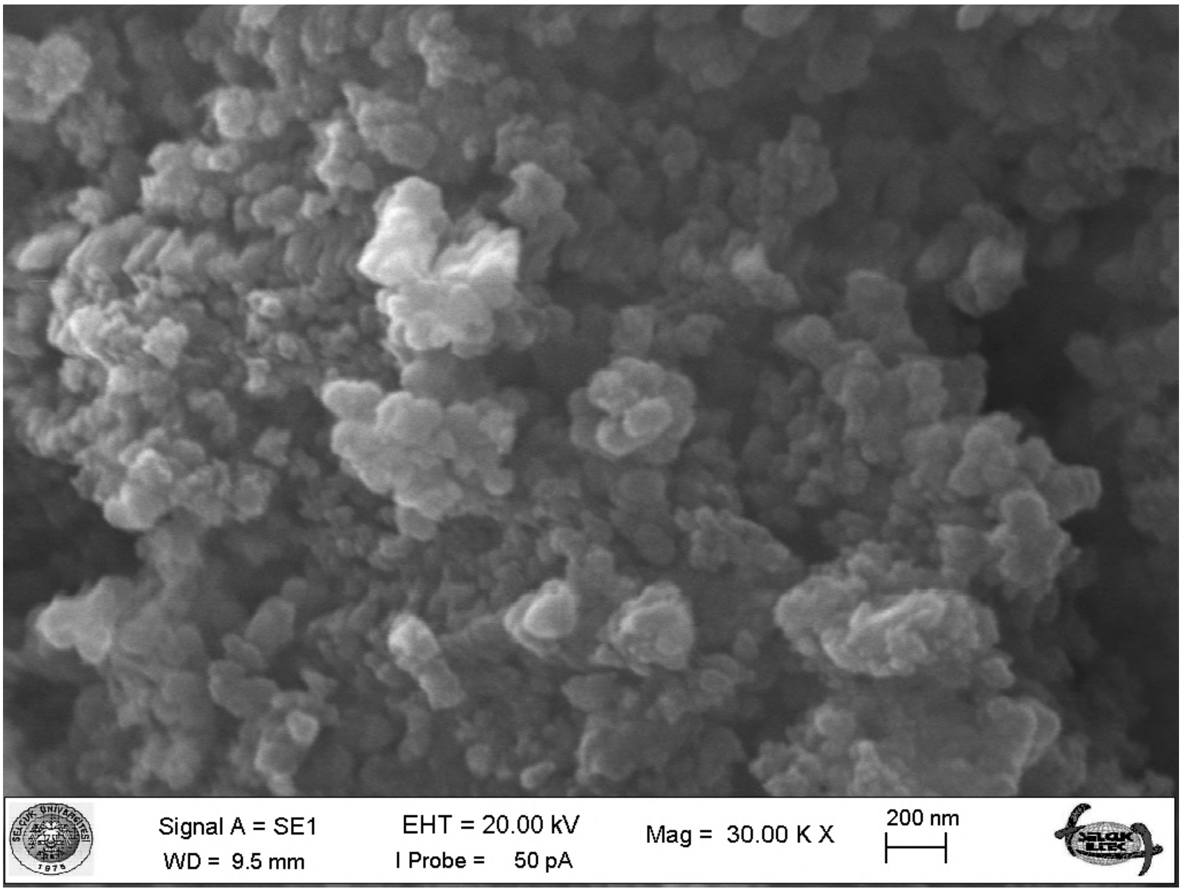

Signal A = SE1
WD = 10.0 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 20.00 K X
200 nm

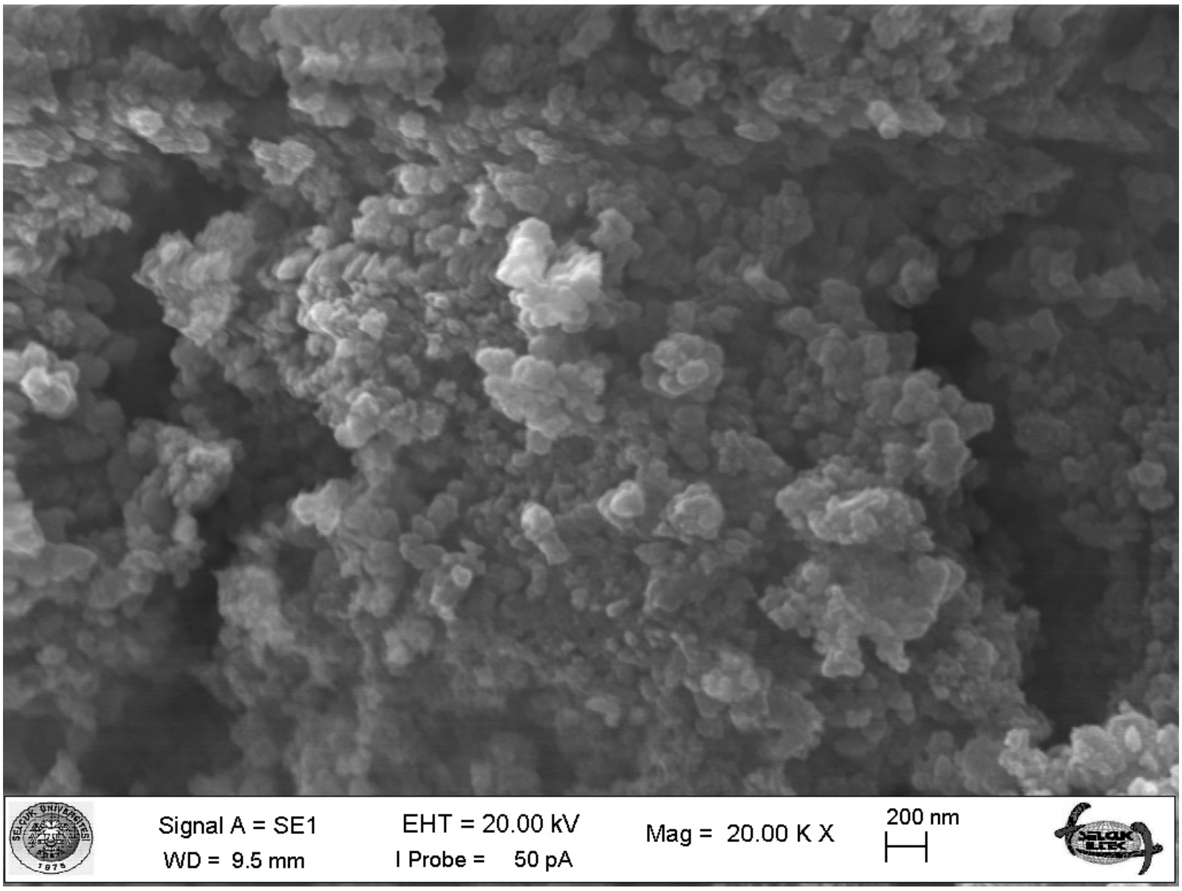

Signal A = SE1
WD = 10.0 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 10.00 K X
1 µm

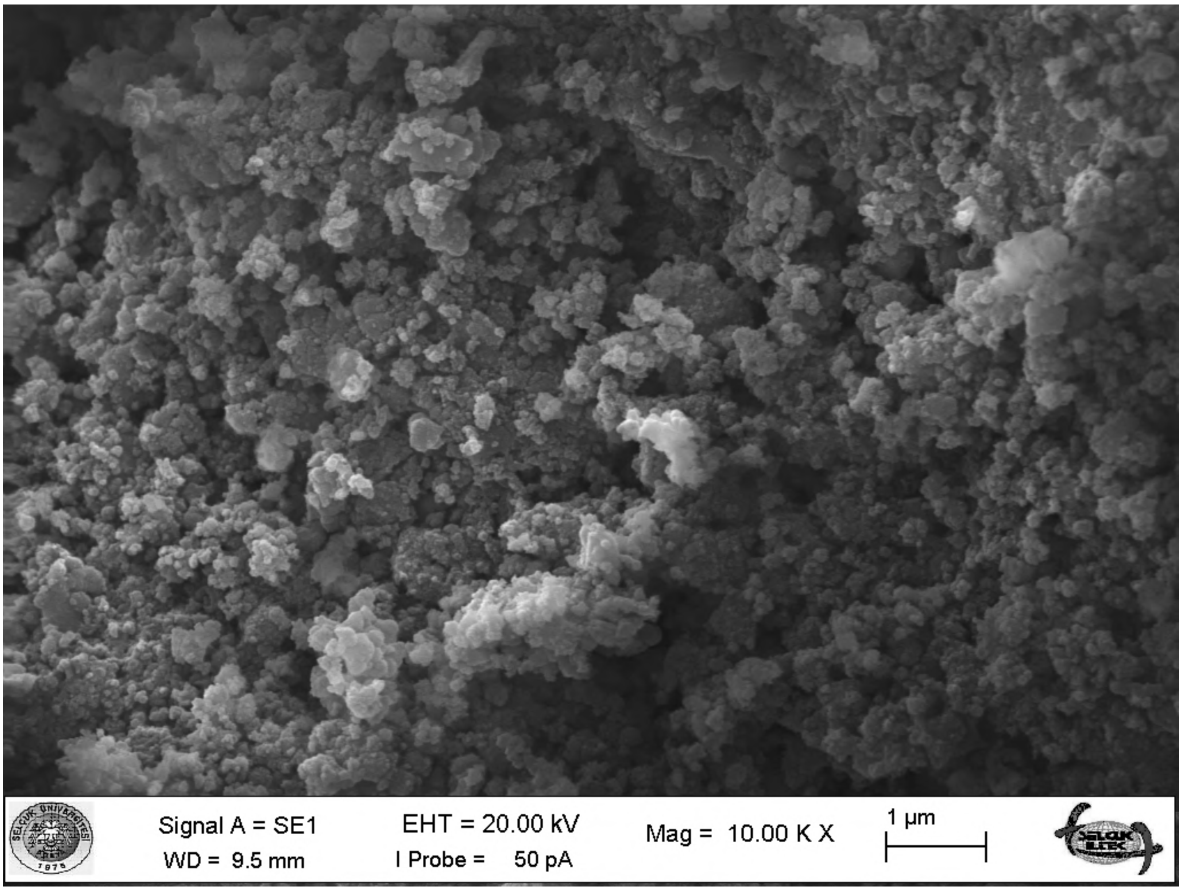

Signal A = SE1
WD = 10.0 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 5.00 K X
1 µm

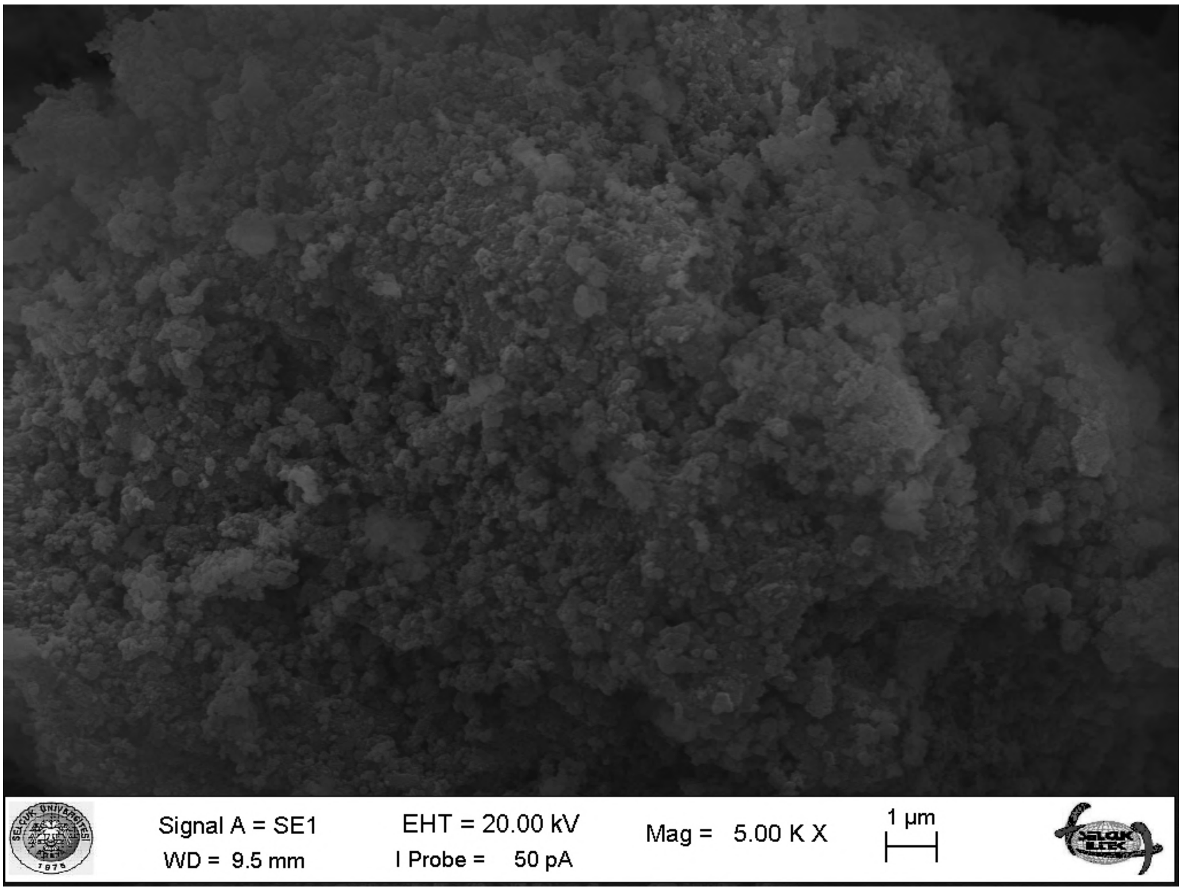

Signal A = SE1
WD = 10.0 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 1.00 K X
10 µm

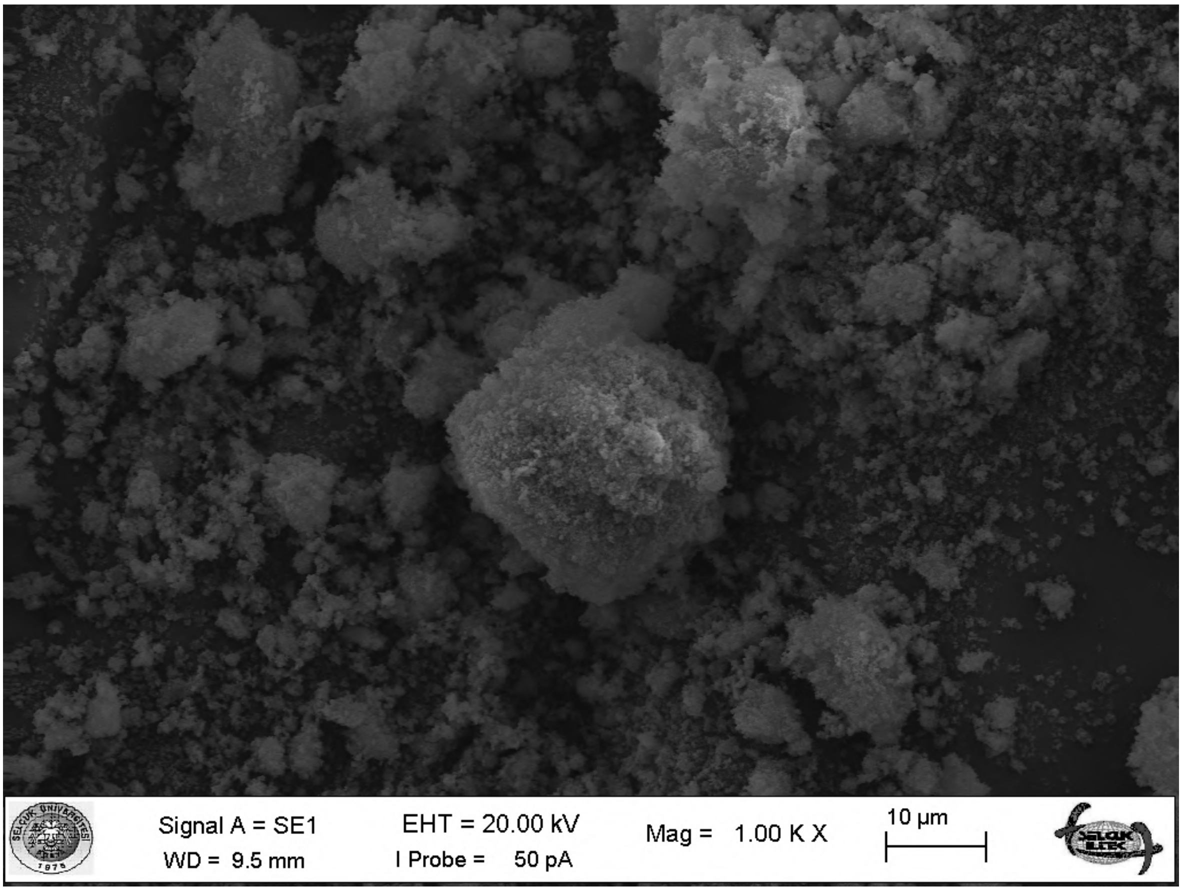
Mengsel:




Signal A = SE1
WD = 9.5 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 20.00 K X
200 nm


Signal A = SE1
WD = 9.5 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 10.00 K X
1 µm


Signal A = SE1
WD = 9.5 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 5.00 K X
1 µm


Signal A = SE1
WD = 9.5 mm
EHT = 20.00 kV
I Probe = 50 pA
Mag = 1.00 K X
10 µm

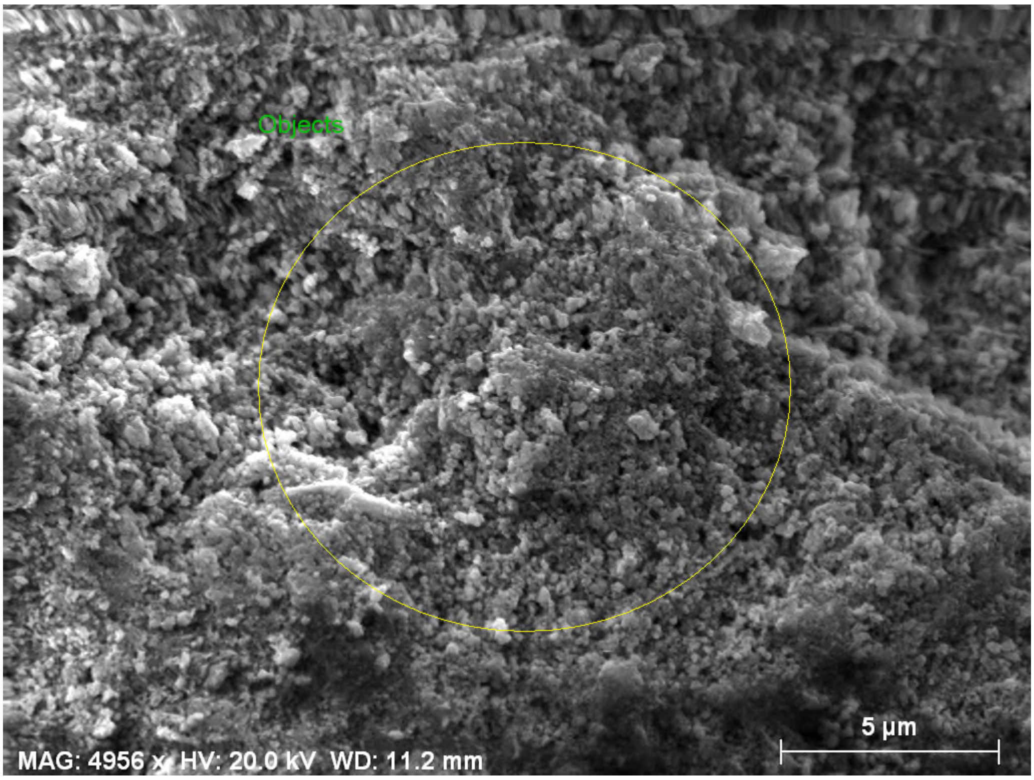
Appendix VI Elemental analysis

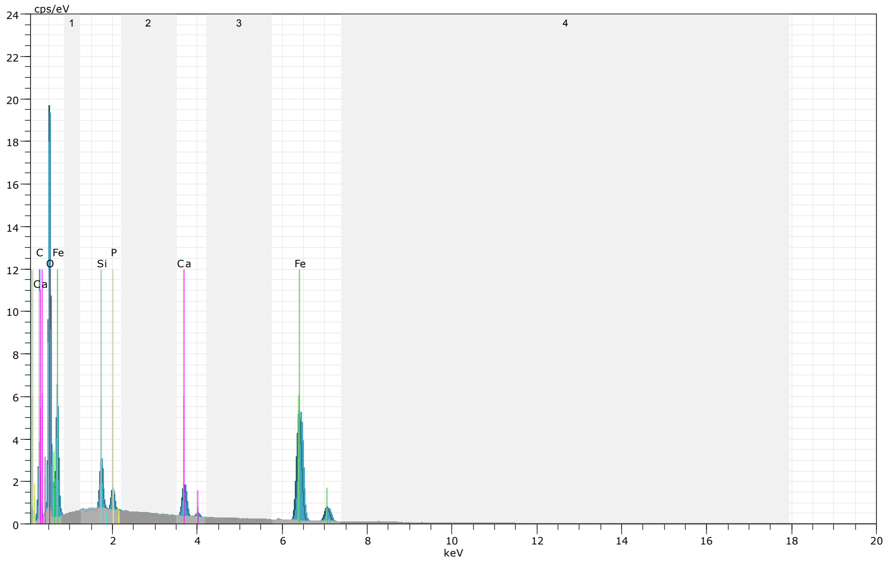
The codes used in the following analytical files are shown in .

code	**Descripton**
Nr. 1 GIH	GIH-pellets used in the Waternet pilot, without CMC, dried at KWR lab before sending for analysis to Agravis
Nr. 2 GIH mit CMC	GIH pellets produced by Agravis and analyzed
Nr.3 GIH ohne CMC	GIH pellets produced by Agravis and analyzed
Nr.4 GIH SPA+	GIH pellets produced at KWR lab from Spannenburg residual having high dose of polymer
Nr. 5 GIH Spa Oud	GIH pellets produced at KWR lab from Spannenburg old residual
Nr. 6 GIH Spa Vers	GIH pellets produced at KWR lab from Spannenburg fresh residual
Nr. 7 GIH Meng	GIH pellets produced at KWR lab from mixed residuals from 11 sites

Appendix VII SEM-EDX results

Pellets from Huijbergen





```
Spectrum: Objects

Element      Series   unn. C norm. C Atom. C Error

                      [wt.%]  [wt.%]  [at.%]   [%]

------------------------------------------------

Oxygen     K-series  51.63   62.40   76.16   6.0

Iron       K-series  20.84   25.19    8.81   0.6

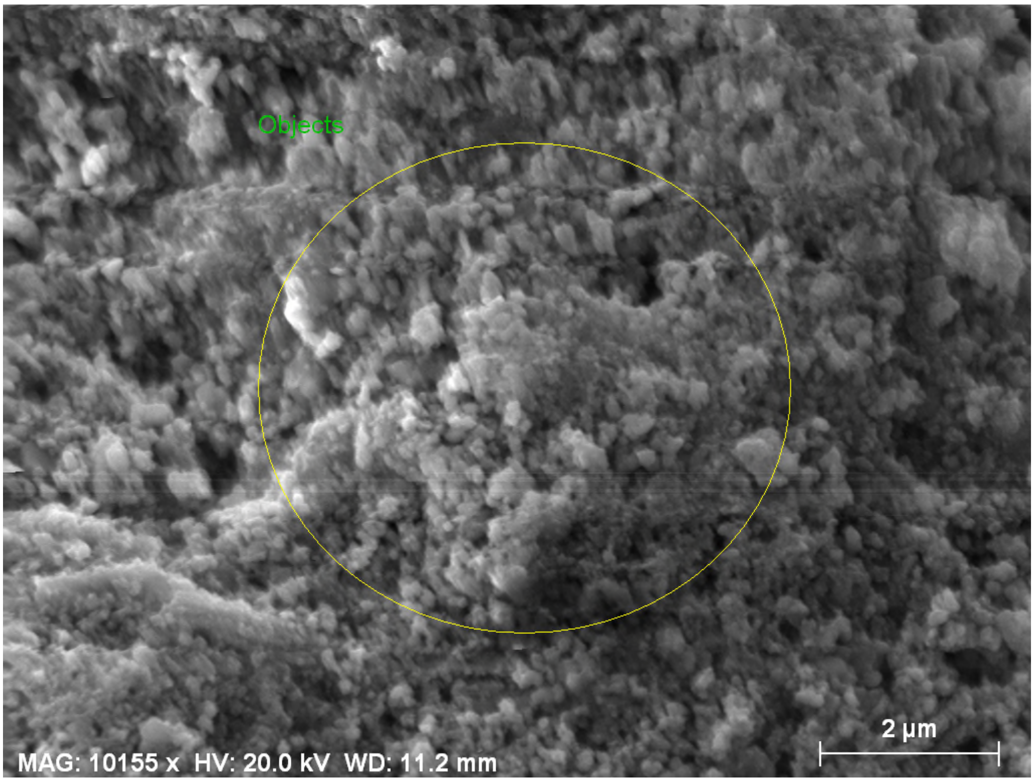
Carbon     K-series   6.22    7.52   12.23   0.9

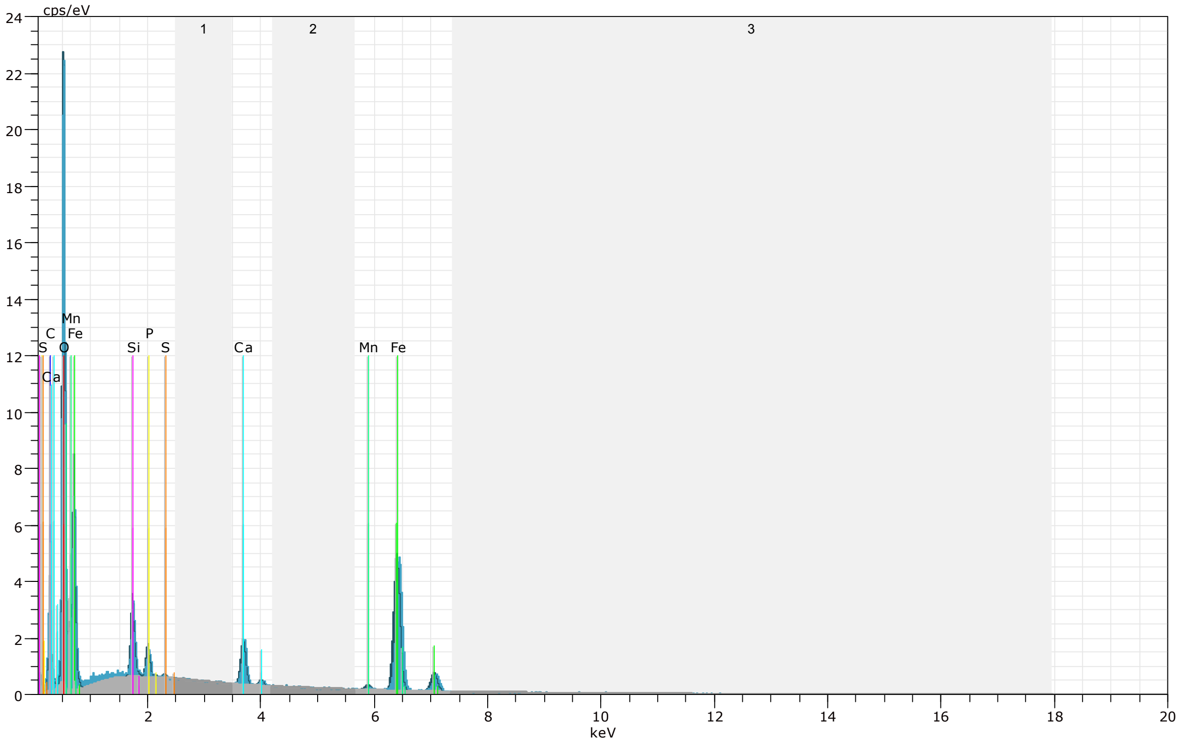
Silicon    K-series   1.22    1.47    1.02   0.1

Calcium    K-series   2.10    2.54    1.24   0.1

Phosphorus K-series   0.72    0.87    0.55   0.1

------------------------------------------------
```





```
Spectrum: Objects


Element     Series   unn. C norm. C Atom. C Error

                     [wt.%]  [wt.%]  [at.%]   [%]

-------------------------------------------------

Oxygen     K-series  55.24   63.66   77.03   6.7

Iron       K-series  19.94   22.98    7.97   0.6

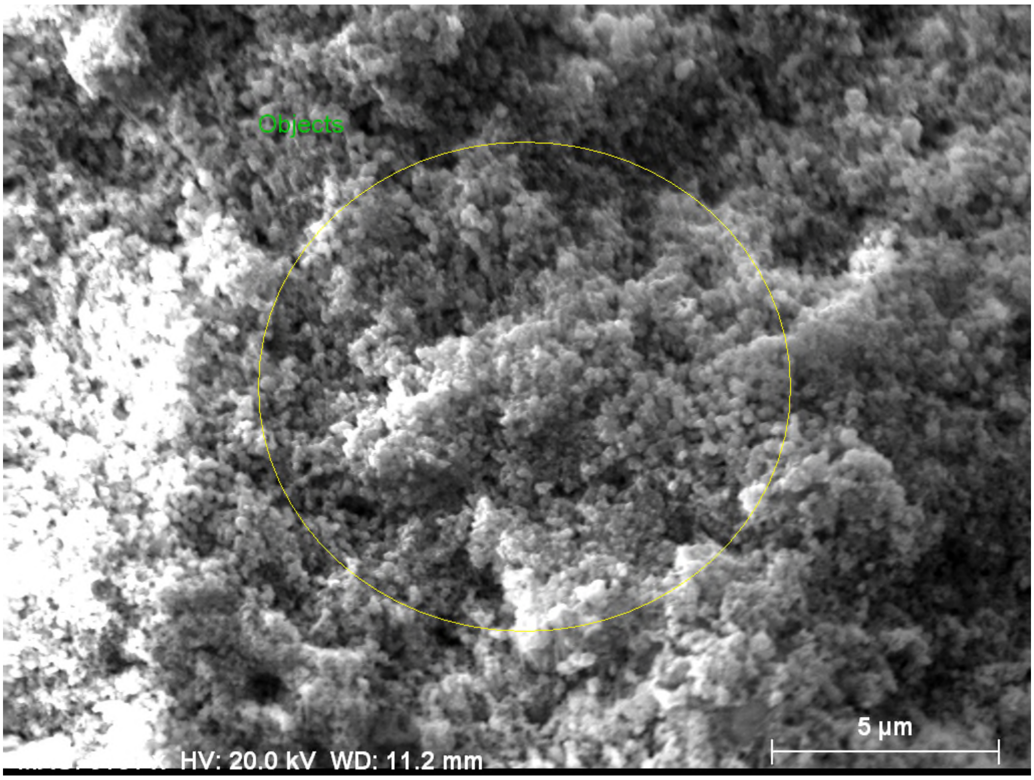
Carbon     K-series   6.21    7.16   11.54   1.0

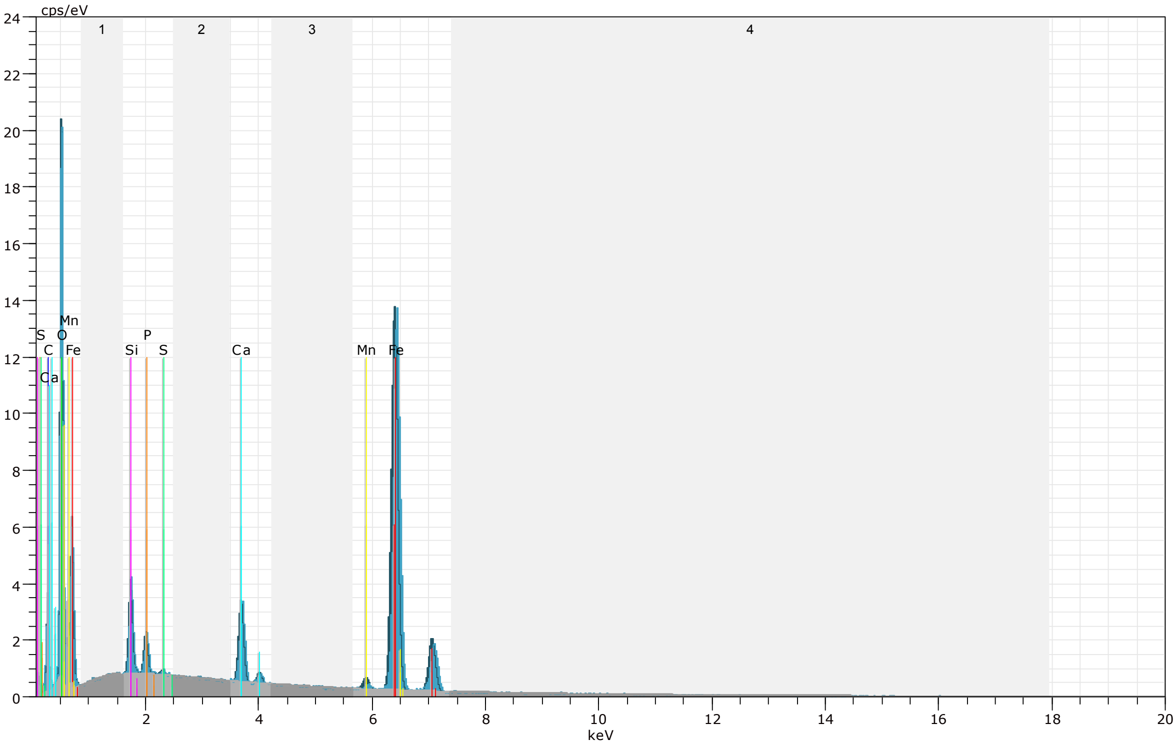
Calcium    K-series   2.11    2.43    1.18   0.1

Silicon    K-series   1.71    1.97    1.36   0.1

Phosphorus K-series   0.84    0.97    0.61   0.1

Sulfur     K-series   0.10    0.11    0.07   0.0
```

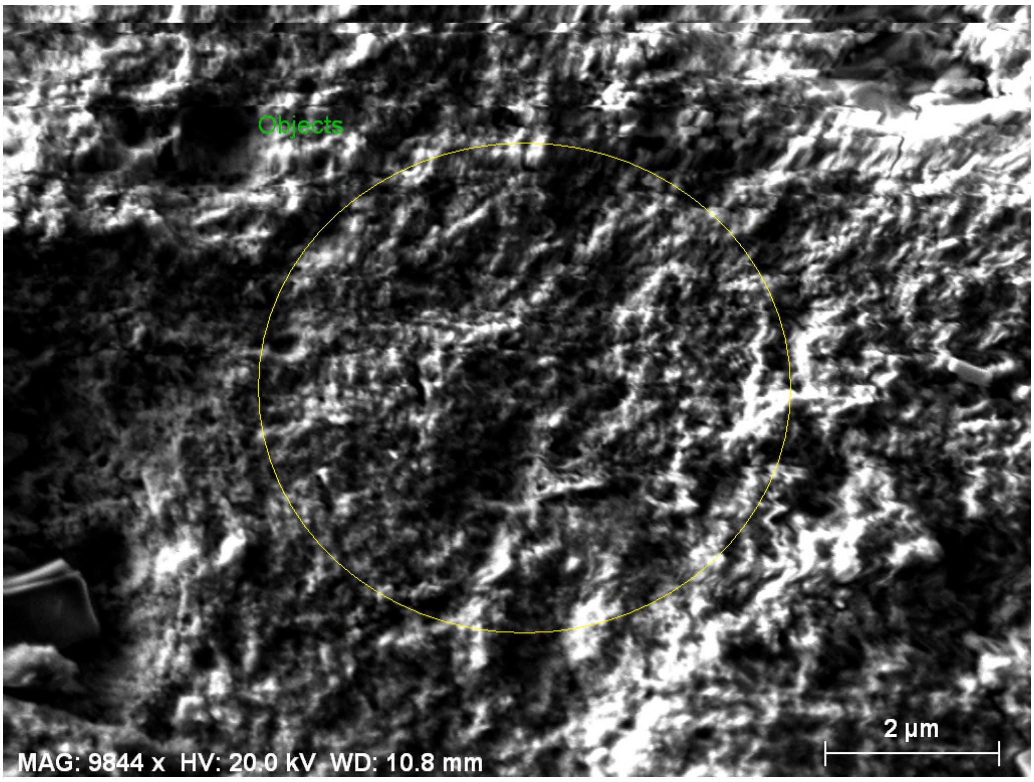

Objects
HV: 20.0 kV WD: 11.2 mm
5 µm

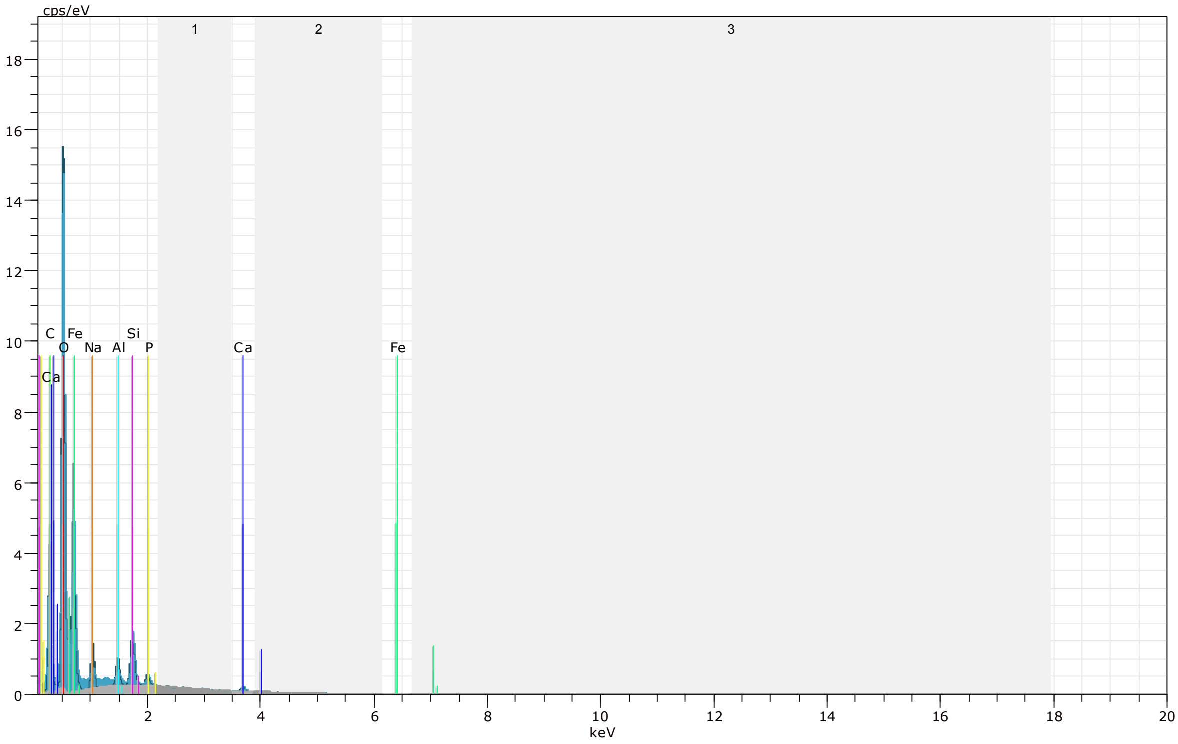

cps/eV
24
22
20
18
16
14
12
10
8
6
4
2
0
1
2
3
4
S
Mn
O
C
Fe
Ca
Si
P
S
Ca
Mn
Fe
2
4
6
8
10
12
14
16
18
20
keV

```
Spectrum: Objects

Element     Series   unn. C norm. C Atom. C Error
                     [wt.%]  [wt.%]  [at.%]   [%]
-------------------------------------------------
Iron       K-series  43.20   47.76   21.74   1.2
Oxygen     K-series  35.71   39.47   62.72   4.5
Carbon     K-series   4.17    4.61    9.76   0.7
Calcium    K-series   3.25    3.59    2.28   0.1
Silicon    K-series   1.91    2.11    1.91   0.1
Manganese  K-series   1.04    1.15    0.53   0.1
Phosphorus K-series   1.04    1.15    0.95   0.1
```

Spannenburg with polyacrylamide 22-1-15





```
Spectrum: Objects


Element     Series  unn. C norm. C Atom. C Error

                    [wt.%]  [wt.%]  [at.%]   [%]

------------------------------------------------

Oxygen     K-series  80.64   80.64   79.67  25.3

Carbon     K-series  12.12   12.12   15.96   4.3

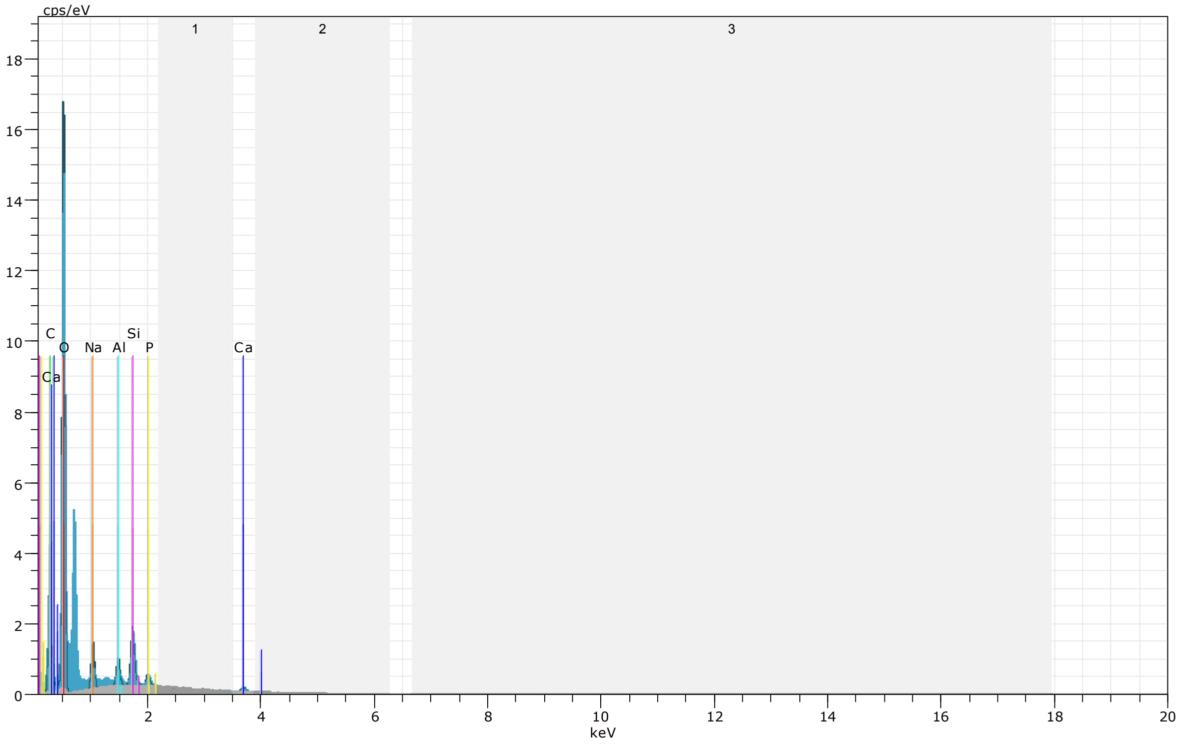
Calcium    K-series   0.61    0.61    0.24   0.1

Aluminium  K-series   1.08    1.08    0.63   0.1

Silicon    K-series   1.80    1.80    1.01   0.1

Phosphorus K-series   0.47    0.47    0.24   0.0

Sodium     K-series   3.26    3.26    2.24   0.2
```



```
Spectrum: Objects


Element     Series   unn. C norm. C Atom. C Error

                     [wt.%]  [wt.%]  [at.%]   [%]

------------------------------------------------

Oxygen     K-series  81.23   81.23   80.43  25.5

Carbon     K-series  11.49   11.49   15.16   4.1

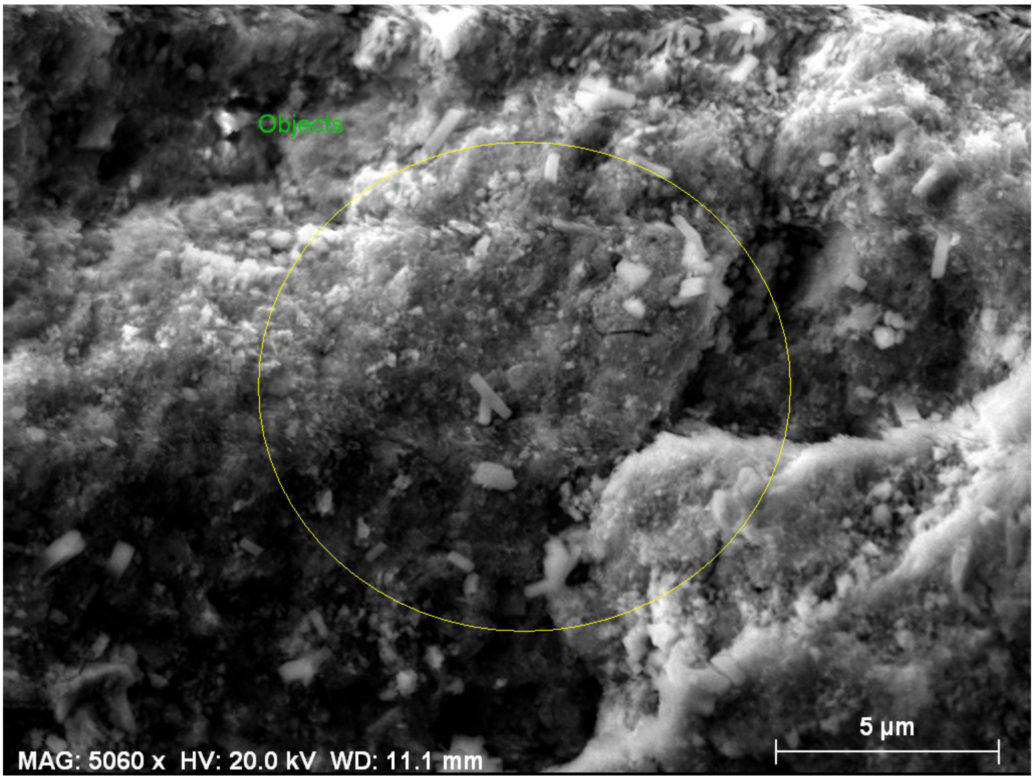
Calcium    K-series   0.63    0.63    0.25   0.1

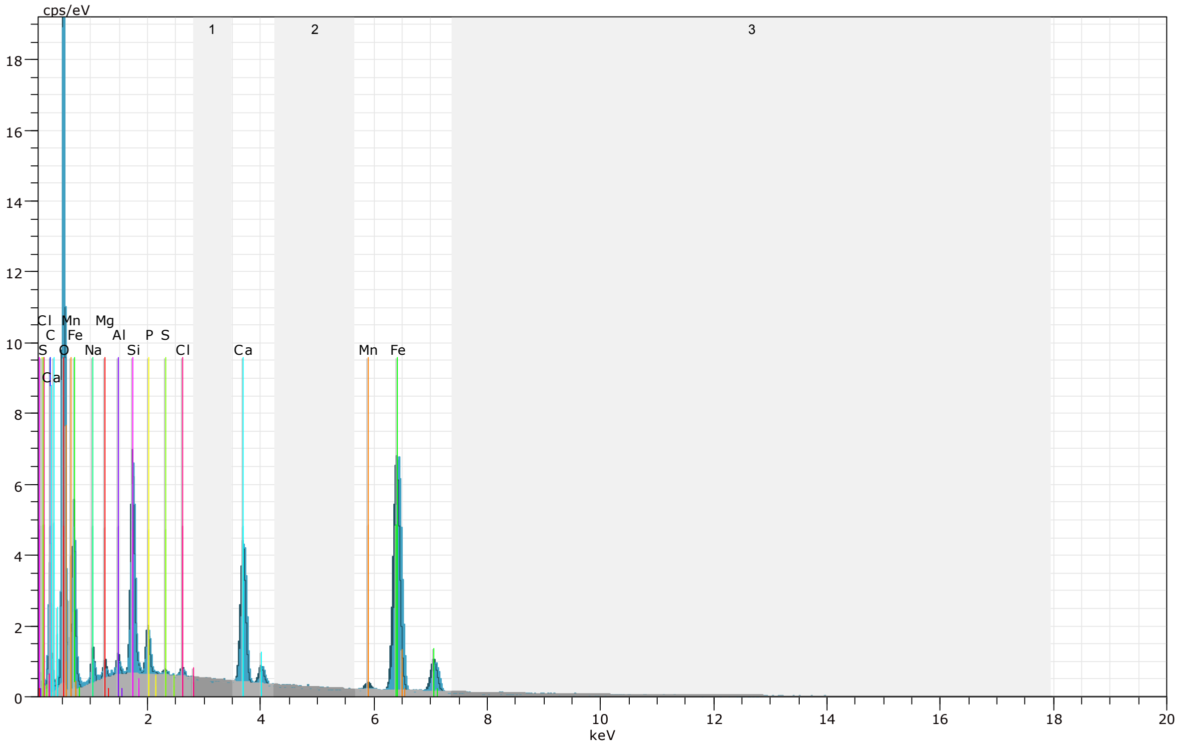
Aluminium  K-series   1.09    1.09    0.64   0.1

Silicon    K-series   1.81    1.81    1.02   0.1

Phosphorus K-series   0.47    0.47    0.24   0.0

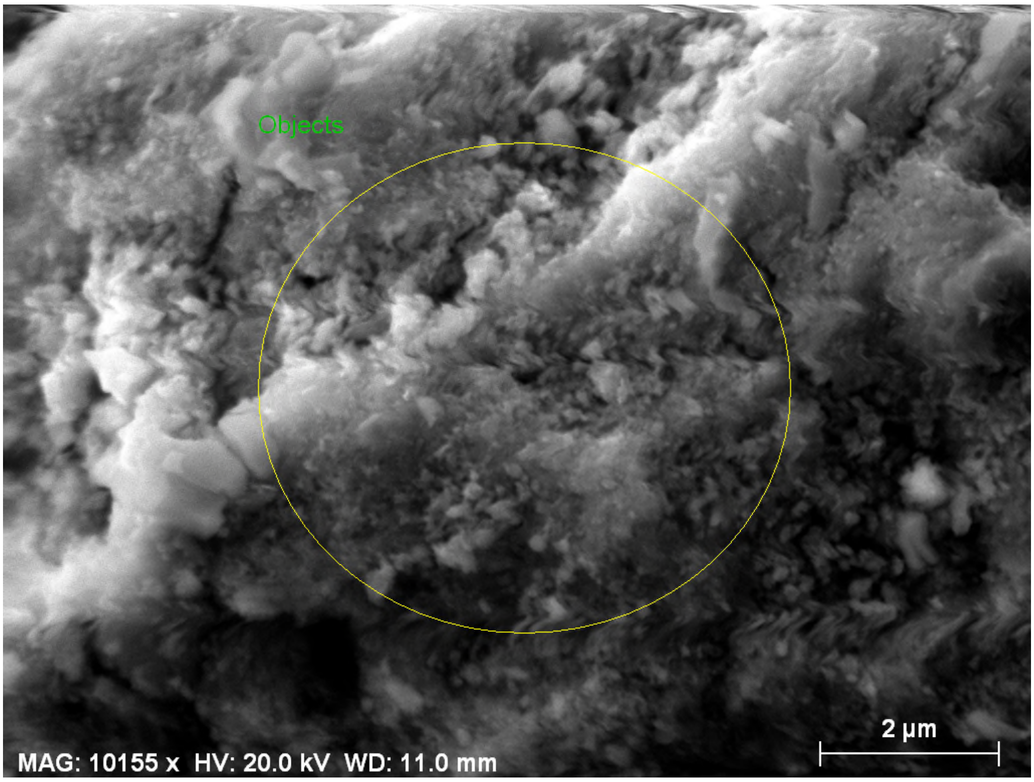
Sodium     K-series   3.29    3.29    2.27   0.3
```

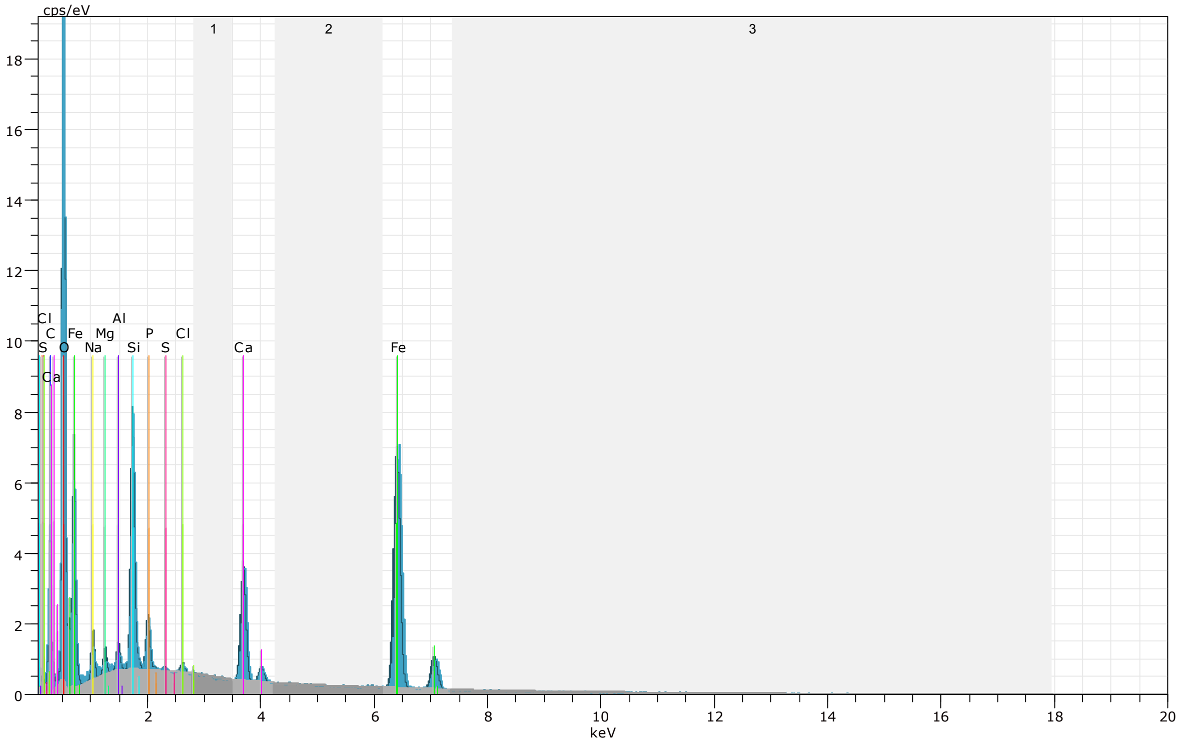

Objects
MAG: 5060 x HV: 20.0 kV WD: 11.1 mm
5 µm


cps/eV
18
16
14
12
10
8
6
4
2
0
1
2
3
Cl Mn Mg
C Fe Al P S
S O Na Si Cl Ca Mn Fe
Ca
2
4
6
8
10
12
14
16
18
20
keV

```
Spectrum: Objects

Element     Series   unn. C norm. C Atom. C Error
                     [wt.%]  [wt.%]  [at.%]   [%]
------------------------------------------------
Oxygen     K-series  45.42   51.06   68.68   5.5
Iron       K-series  24.82   27.90   10.75   0.7
Carbon     K-series   4.96    5.57    9.98   1.0
Calcium    K-series   5.00    5.61    3.02   0.2
Silicon    K-series   3.95    4.44    3.40   0.2
Phosphorus K-series   1.09    1.22    0.85   0.1
Manganese  K-series   0.63    0.71    0.28   0.1
```





```
Spectrum: Objects


Element      Series   unn. C norm. C Atom. C Error

                      [wt.%]  [wt.%]  [at.%]    [%]

-------------------------------------------------

Oxygen     K-series   48.34    54.19   70.56   5.8

Iron       K-series   22.88    25.65    9.57   0.6

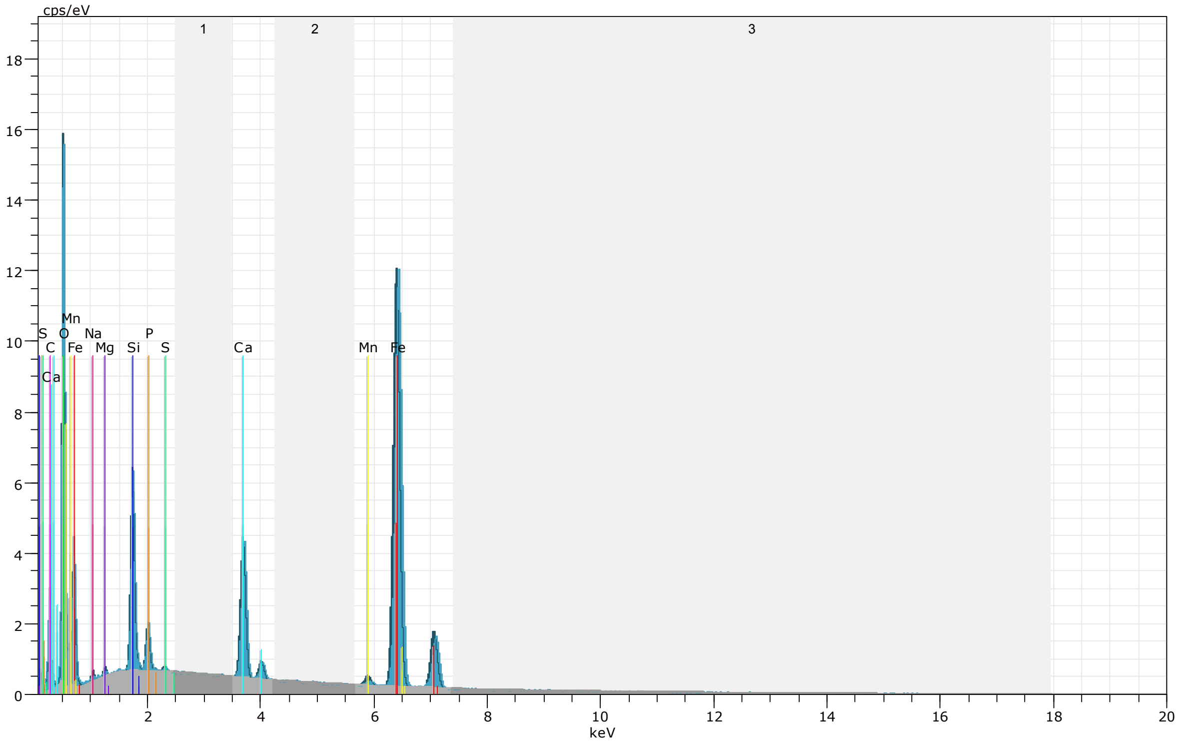
Carbon     K-series    5.05     5.66    9.82   1.0

Silicon    K-series    4.08     4.57    3.39   0.2

Calcium    K-series    4.22     4.73    2.46   0.2

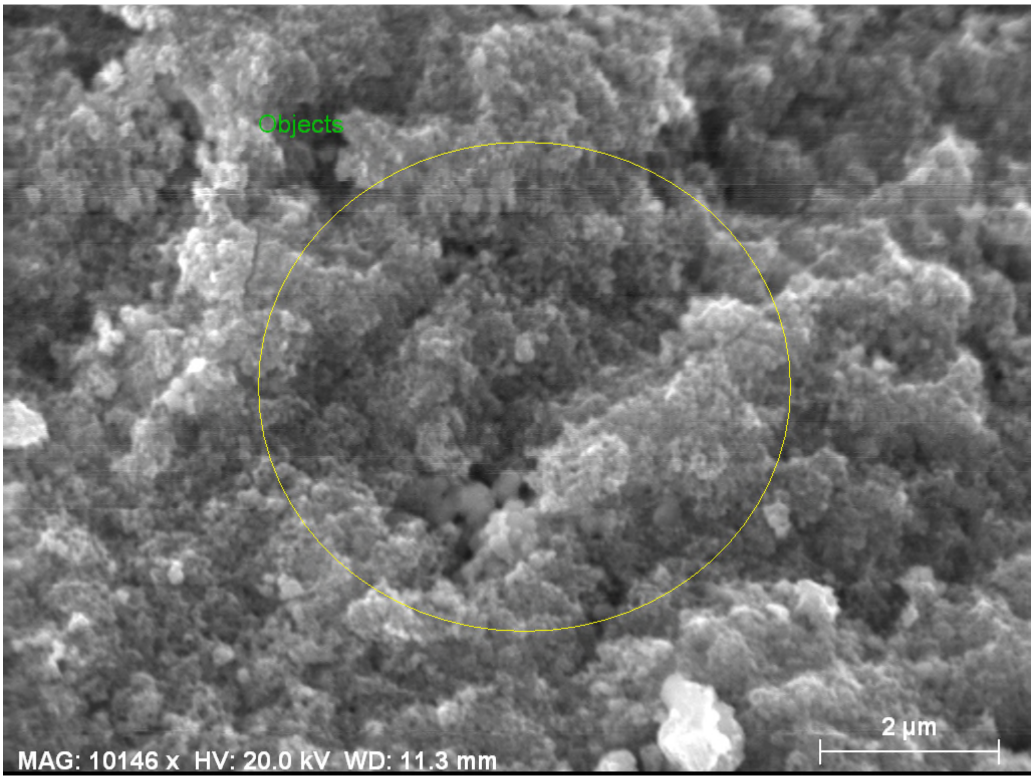
Sodium     K-series    1.98     2.22    2.01   0.2

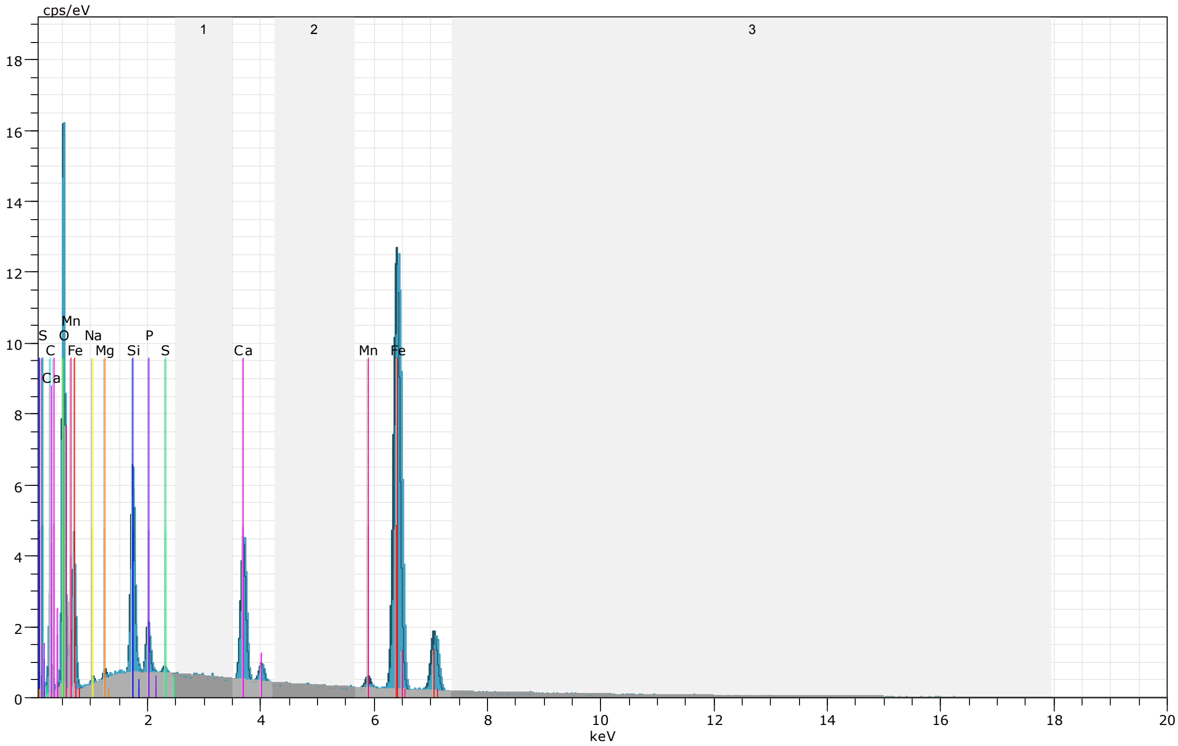
Phosphorus K-series    1.08     1.21    0.81   0.1
```



Spectrum: Objects

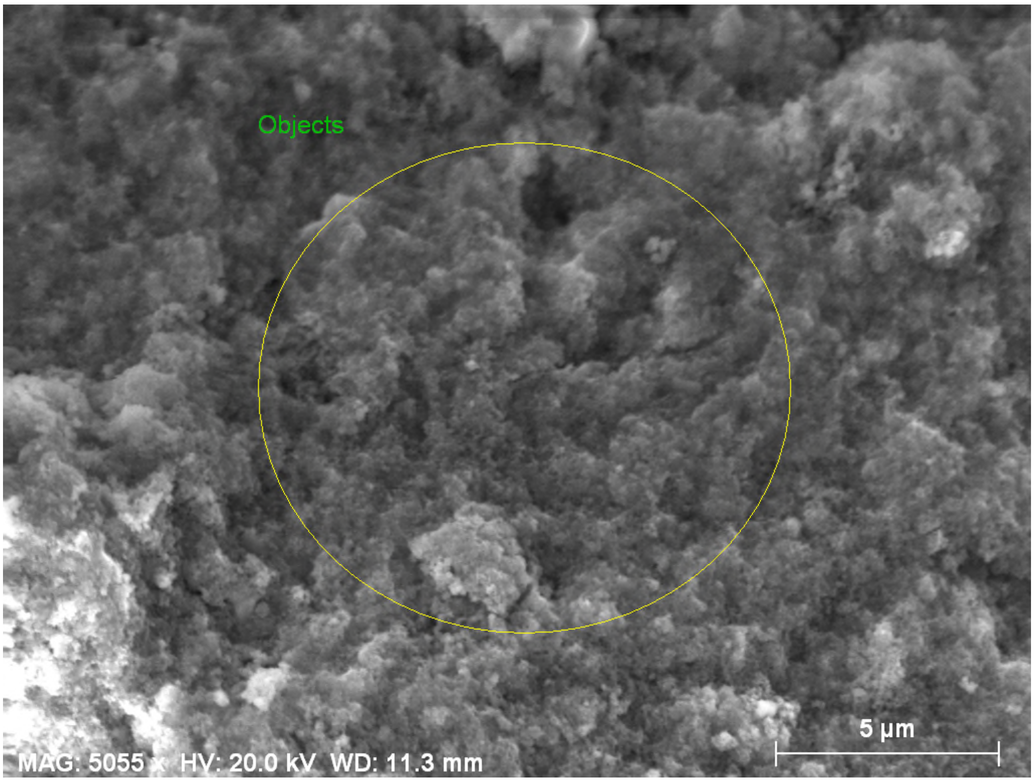
Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Iron	K-series	40.44	45.58	21.08	1.1
Oxygen	K-series	32.54	36.68	59.20	3.8
Silicon	K-series	4.00	4.51	4.15	0.2
Calcium	K-series	5.01	5.64	3.64	0.2
Carbon	K-series	3.80	4.28	9.20	0.6
Manganese	K-series	0.73	0.82	0.39	0.1
Phosphorus	K-series	1.15	1.30	1.08	0.1

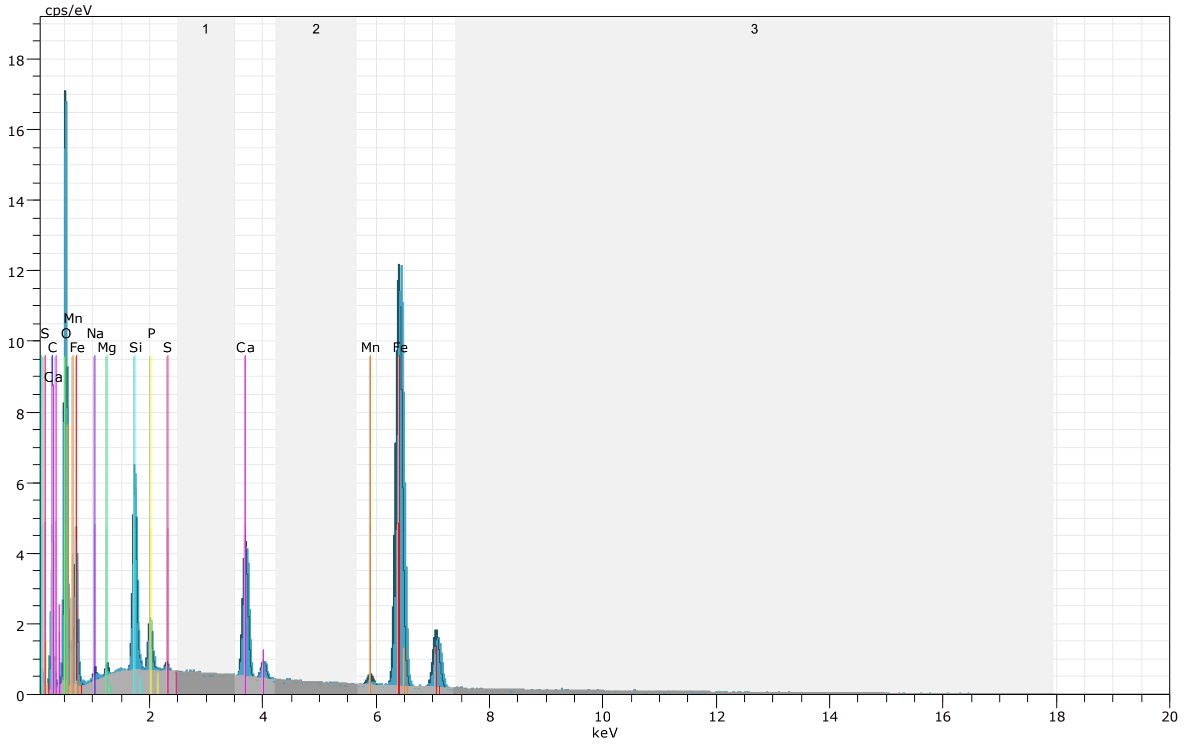

Objects
2 µm
MAG: 10146 x HV: 20.0 kV WD: 11.3 mm


cps/eV
18
16
14
12
10
8
6
4
2
0
1
2
3
S
Mn
O
Na
P
C
Fe
Mg
Si
S
Ca
Ca
Mn
Fe
2
4
6
8
10
12
14
16
18
20
keV

```
Spectrum: Objects

Element     Series   unn. C norm. C Atom. C Error
                     [wt.%]  [wt.%]  [at.%]   [%]
-------------------------------------------------
Iron        K-series  41.73   46.74   21.95   1.2
Oxygen      K-series  31.94   35.77   58.65   4.1
Silicon     K-series   4.01    4.49    4.19   0.2
Carbon      K-series   3.59    4.02    8.78   0.7
Calcium     K-series   4.85    5.43    3.55   0.2
Sodium      K-series   0.49    0.55    0.63   0.1
Magnesium   K-series   0.36    0.40    0.43   0.1
```





```
Spectrum: Objects


Element      Series   unn. C norm. C Atom. C Error

                      [wt.%]  [wt.%]  [at.%]    [%]

-----------------------------------------------

Iron       K-series  40.46   44.70   20.46   1.1

Oxygen     K-series  33.39   36.88   58.94   4.4

Carbon     K-series   4.16    4.59    9.78   0.8

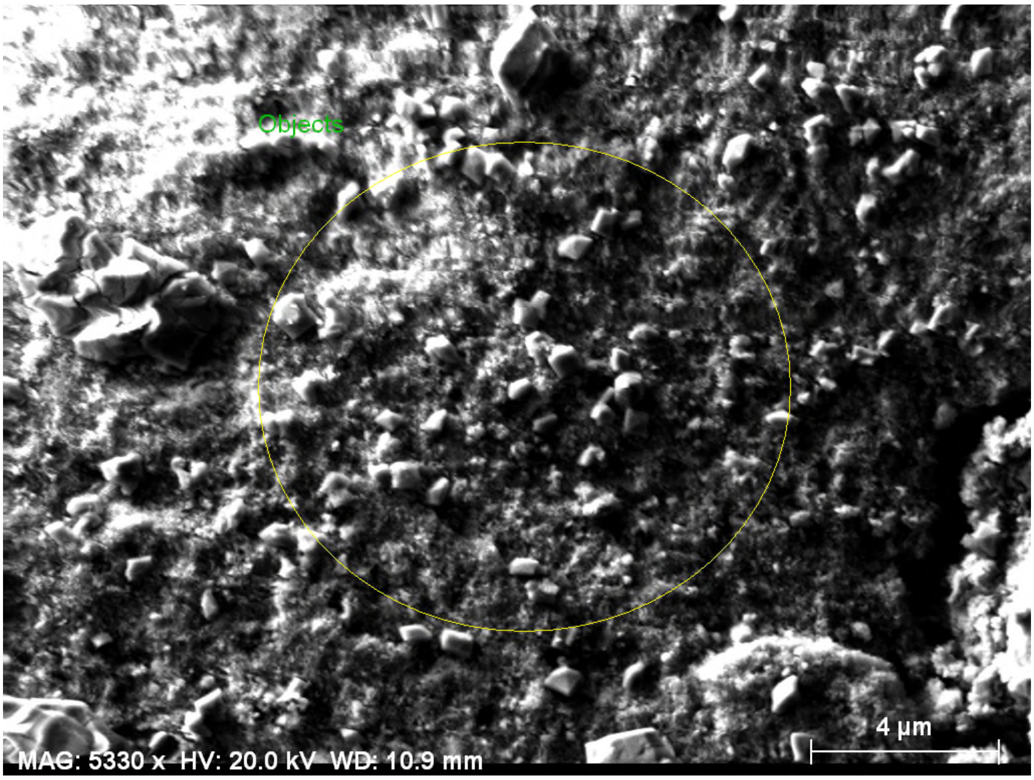
Silicon    K-series   4.03    4.46    4.06   0.2

Calcium    K-series   4.79    5.29    3.37   0.2

Phosphorus K-series   1.28    1.41    1.16   0.1

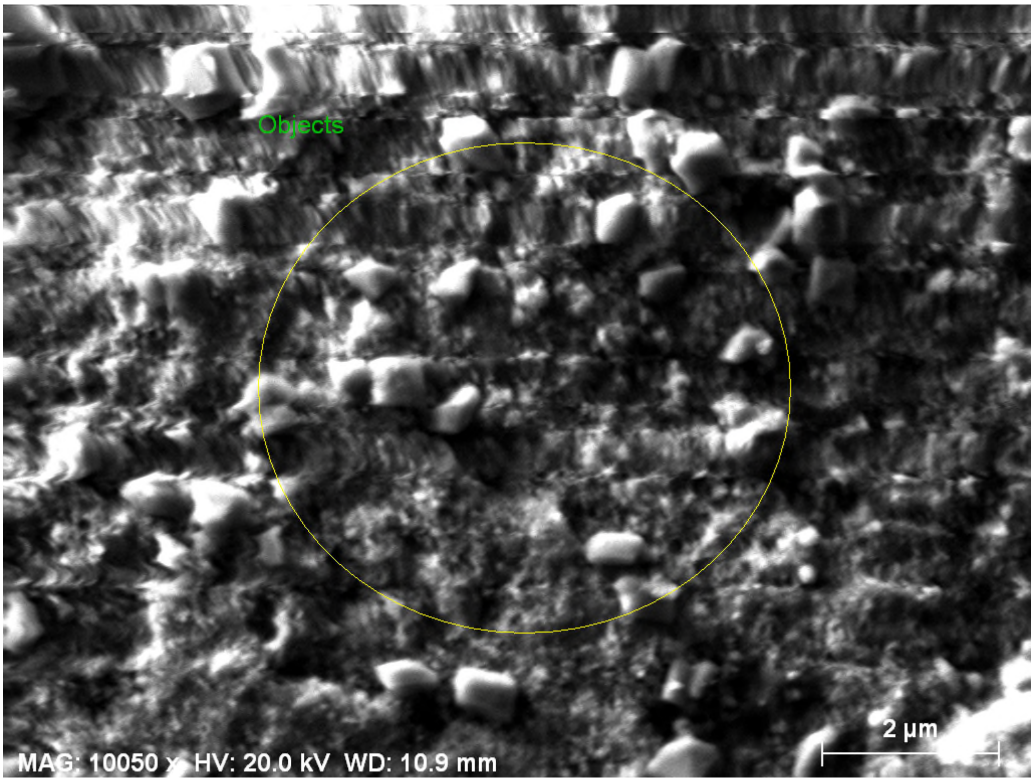
Manganese  K-series   0.88    0.98    0.45   0.1
```

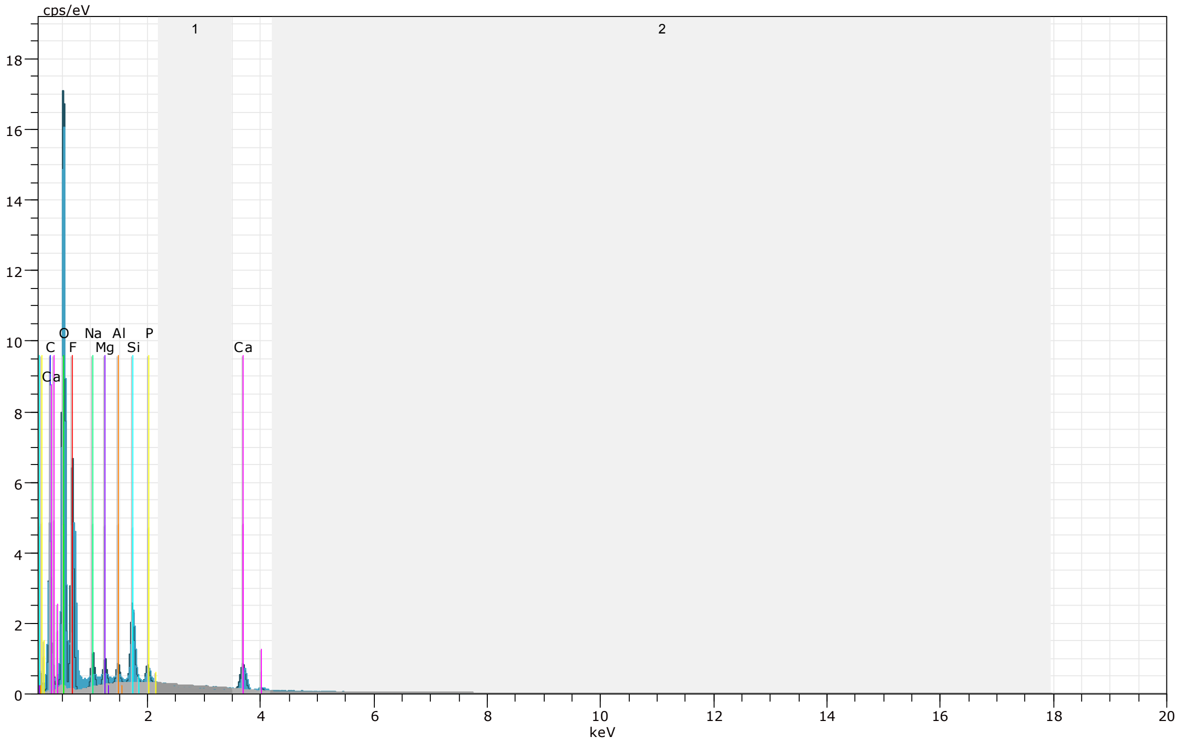
Ferrosorp



```
Spectrum: Objects

Element      Series   unn. C norm. C Atom. C Error
                      [wt.%]  [wt.%]  [at.%]   [%]
------------------------------------------------
Oxygen     K-series  78.83   78.84   78.20  24.7
Carbon     K-series  13.30   13.30   17.57   4.7
Calcium    K-series   1.80    1.80    0.71   0.1
Silicon    K-series   1.79    1.79    1.01   0.1
Iron       K-series   0.67    0.67    0.19   0.1
Phosphorus K-series   0.49    0.49    0.25   0.0
Magnesium  K-series   0.88    0.88    0.57   0.1
```





```
Spectrum: Objects


Element      Series   unn. C norm. C Atom. C Error

                      [wt.%]  [wt.%]  [at.%]    [%]

------------------------------------------------

Fluorine    K-series  53.02   53.02   49.80  17.2

Oxygen      K-series  32.06   32.06   35.76  10.4

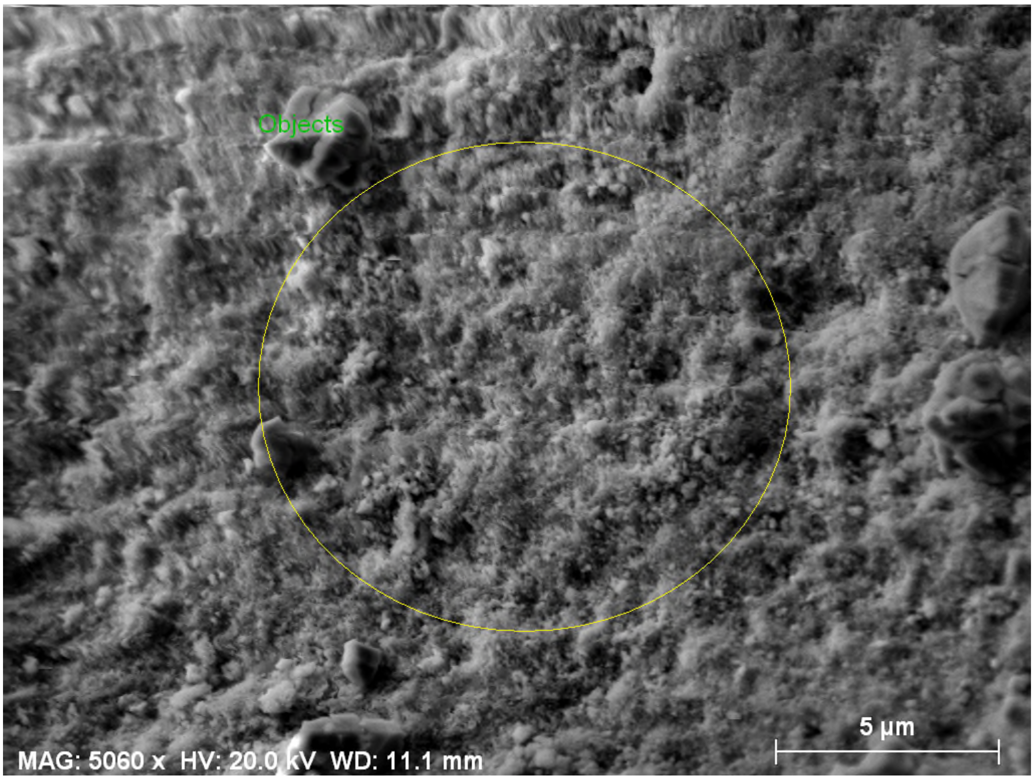
Carbon      K-series   5.90    5.90    8.76   2.4

Silicon     K-series   2.05    2.05    1.30   0.1

Calcium     K-series   2.40    2.40    1.07   0.1

Phosphorus  K-series   0.60    0.60    0.34   0.1

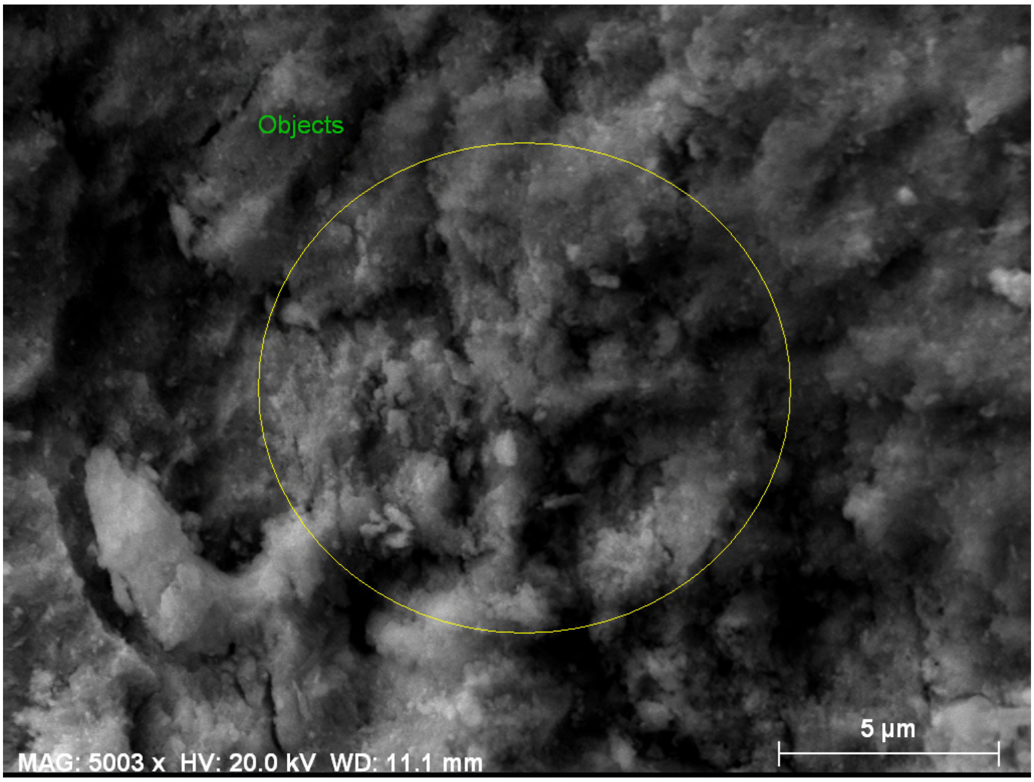
Aluminium   K-series   0.67    0.67    0.44   0.1
```

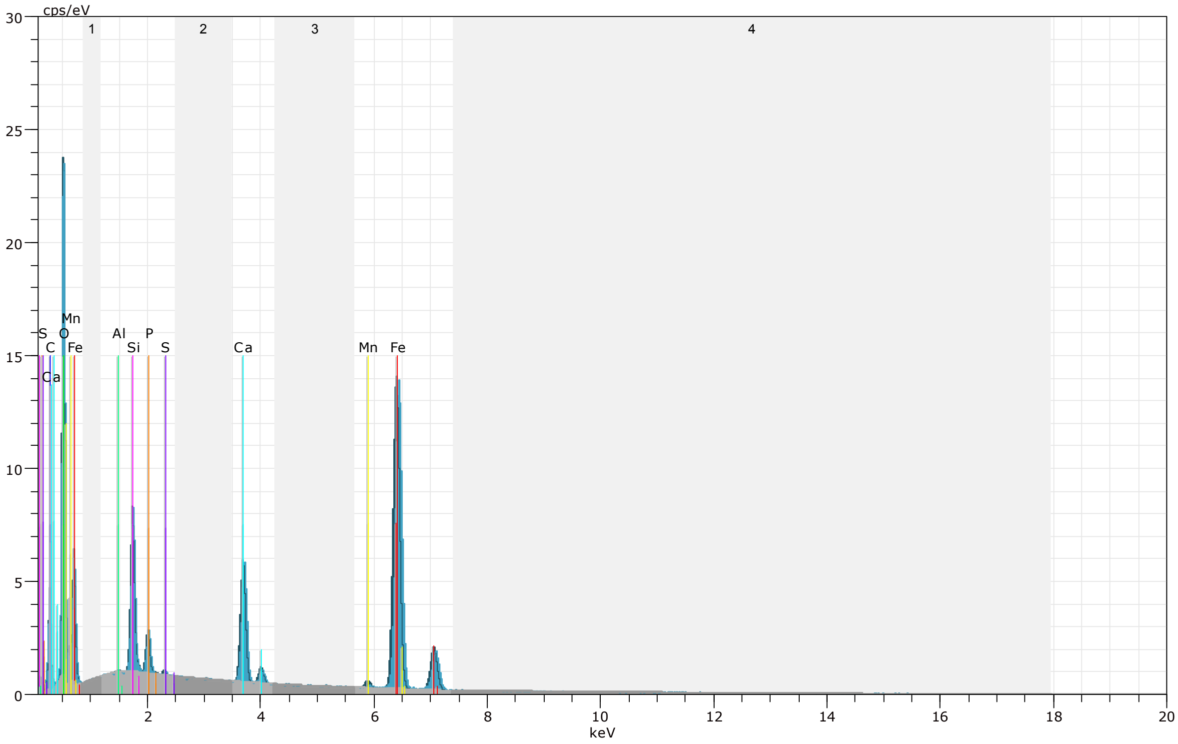

Objects
MAG: 5060 x HV: 20.0 kV WD: 11.1 mm
5 µm

```
Spectrum: Objects

Element      Series   unn. C norm. C Atom. C Error
                      [wt.%]  [wt.%]  [at.%]   [%]
-------------------------------------------------
Oxygen     K-series  79.79   79.79   80.38  25.0
Carbon     K-series  12.34   12.34   16.55   4.3
Iron       K-series   3.85    3.85    1.11   0.2
Silicon    K-series   1.62    1.62    0.93   0.1
Calcium    K-series   1.92    1.92    0.77   0.1
Phosphorus K-series   0.48    0.48    0.25   0.0
-------------------------------------------------
```

Agravis





```
Spectrum: Objects


Element      Series   unn. C norm. C Atom. C Error

                      [wt.%]  [wt.%]  [at.%]   [%]

-------------------------------------------------

Iron        K-series  41.62   44.09   19.80   1.1

Oxygen      K-series  37.25   39.46   61.87   4.4

Carbon      K-series   4.51    4.78    9.98   0.7

Calcium     K-series   5.70    6.04    3.78   0.2

Silicon     K-series   3.30    3.50    3.12   0.2

Manganese   K-series   0.74    0.78    0.36   0.1

Phosphorus K-series    1.10    1.16    0.94   0.1
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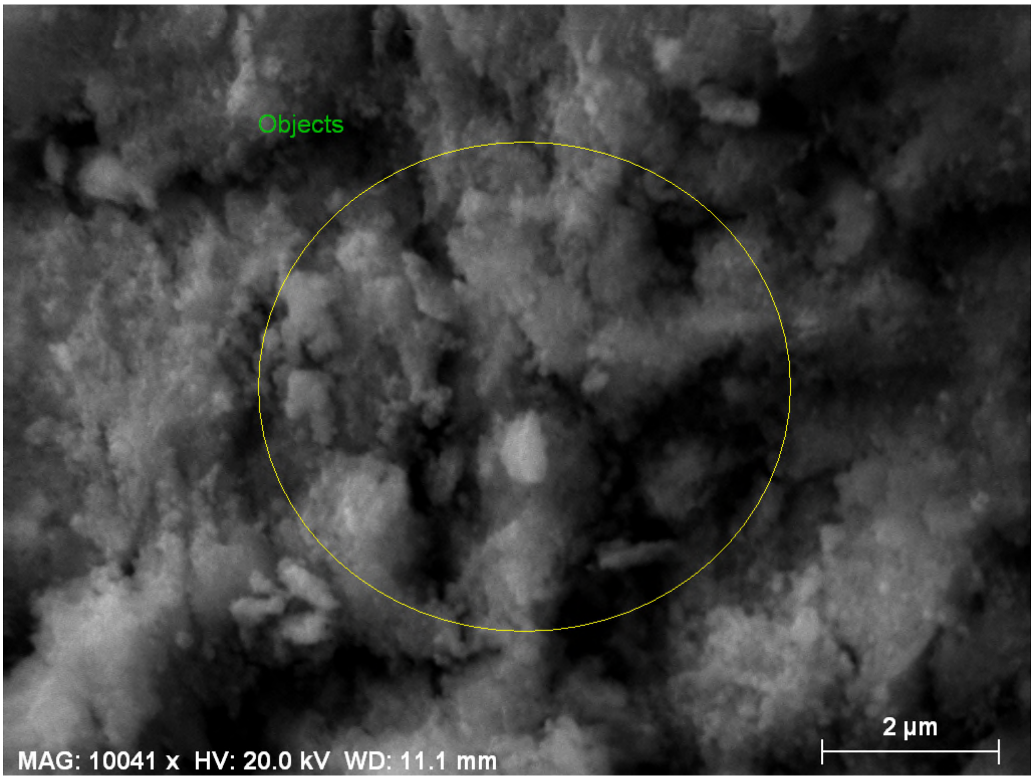
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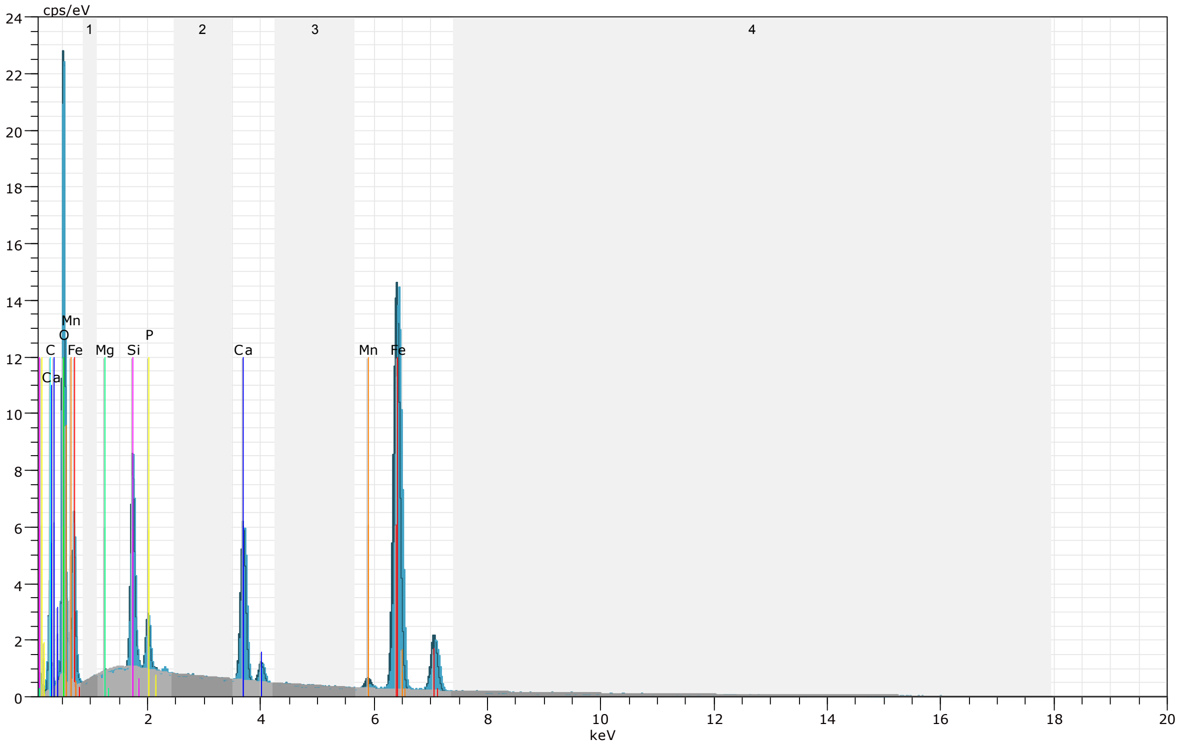
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C
Fe
Mg
Si
P
Ca
Ca
Mn
Fe
2
4
6
8
10
12
14
16
18
20
keV

```
Spectrum: Objects


Element      Series   unn. C norm. C Atom. C Error

                      [wt.%]  [wt.%]  [at.%]   [%]

------------------------------------------------

Iron        K-series  44.35   46.47   21.57   1.2

Oxygen      K-series  35.73   37.44   60.66   4.3

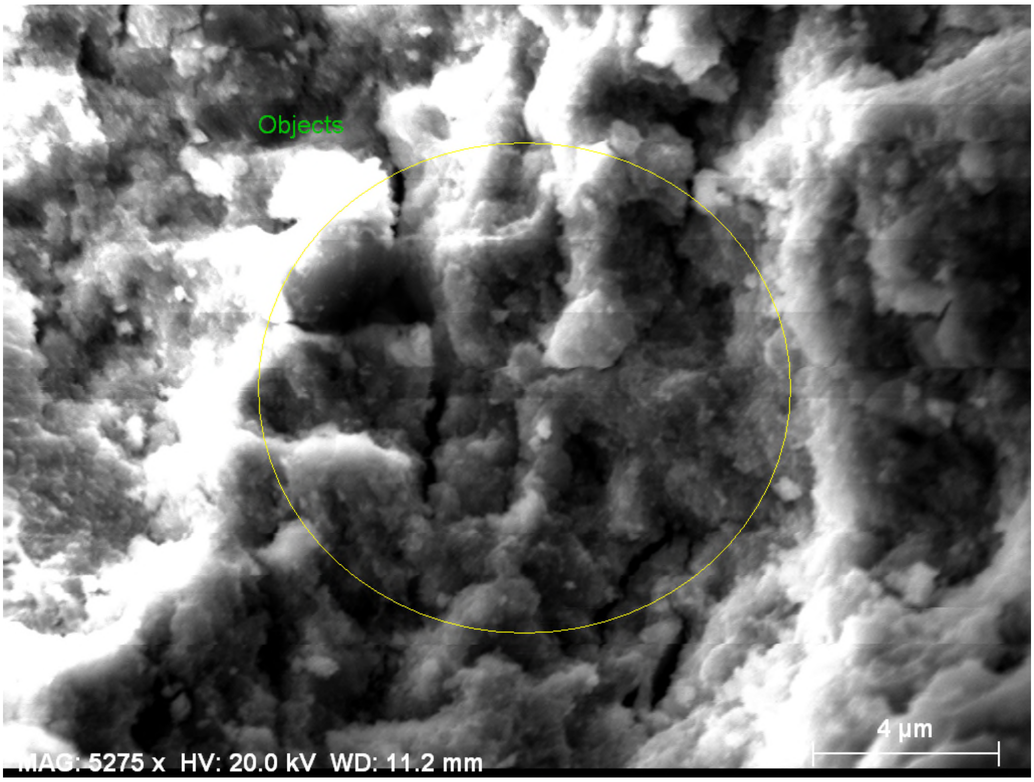
Calcium     K-series   5.84    6.12    3.96   0.2

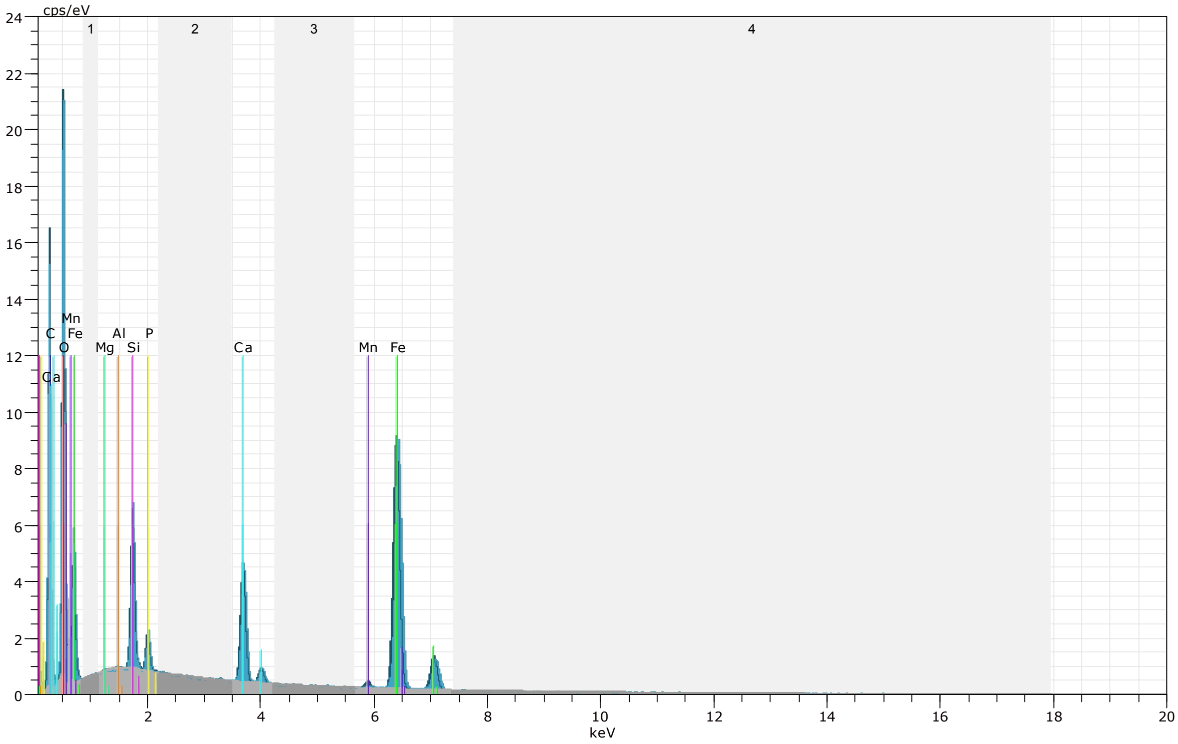
Carbon      K-series   3.97    4.16    8.99   0.6

Silicon     K-series   3.38    3.55    3.27   0.2

Phosphorus K-series   1.18    1.24    1.04   0.1

Manganese   K-series   0.93    0.98    0.46   0.1
```





```
Spectrum: Objects


Element      Series   unn. C norm. C Atom. C Error

                      [wt.%]  [wt.%]  [at.%]   [%]

------------------------------------------------

Oxygen     K-series  43.42   45.13   56.72   5.3

Iron       K-series  28.30   29.42   10.59   0.8

Carbon     K-series  15.86   16.48   27.60   2.1

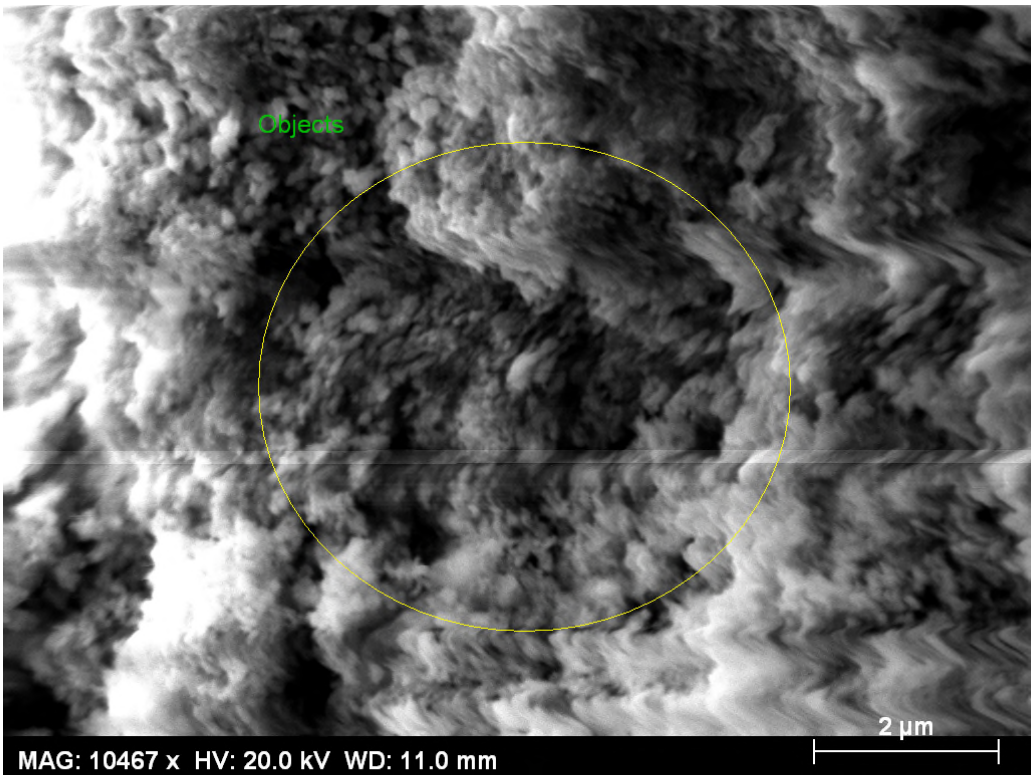
Calcium    K-series   4.76    4.94    2.48   0.2

Silicon    K-series   2.38    2.48    1.77   0.1

Phosphorus K-series   0.82    0.85    0.56   0.1

Aluminium  K-series   0.02    0.02    0.02   0.0
```

Mixture 22-1-15



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Spectrum: Objects


Element     Series   unn. C norm. C Atom. C Error

                     [wt.%]  [wt.%]  [at.%]   [%]

------------------------------------------------

Oxygen     K-series  71.99   71.99   78.70  22.7

Iron       K-series  13.71   13.71    4.29   0.4

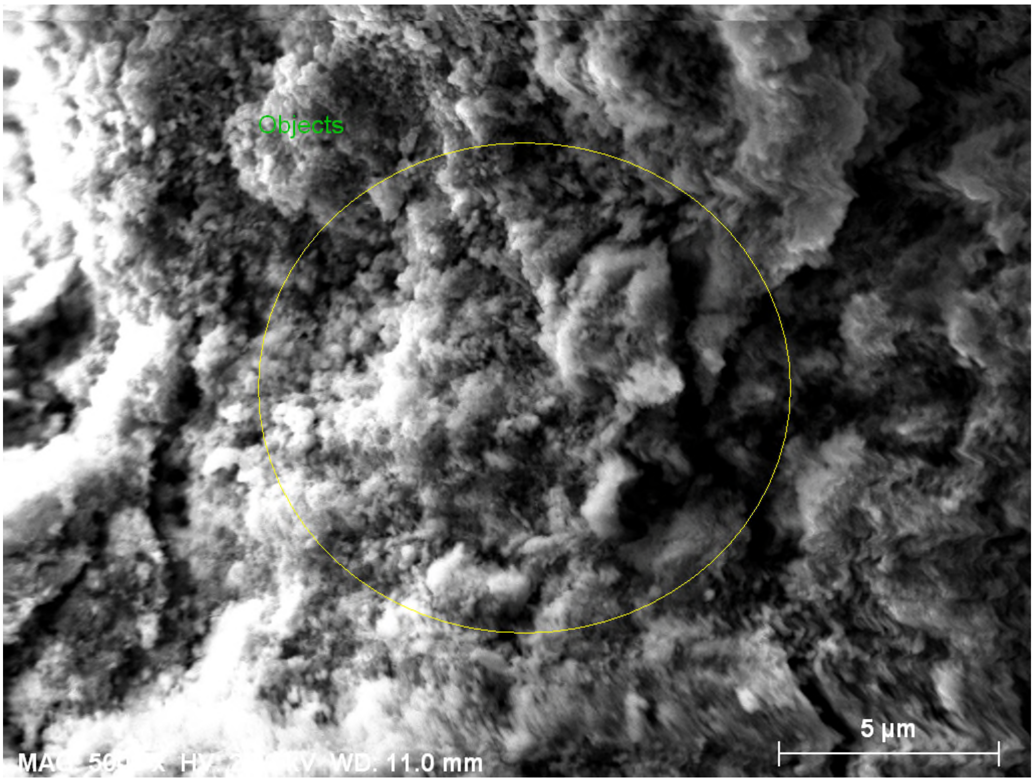
Carbon     K-series  10.30   10.30   14.99   3.9

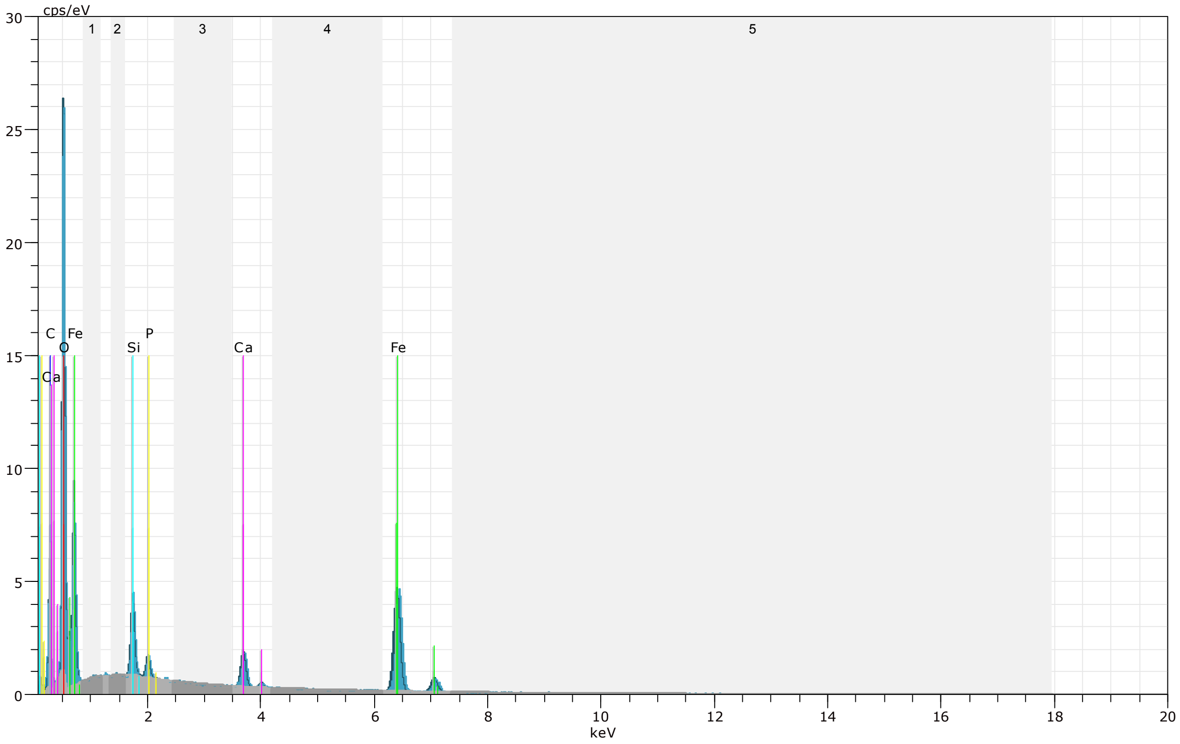
Silicon    K-series   1.38    1.38    0.86   0.1

Calcium    K-series   1.63    1.63    0.71   0.1

Manganese  K-series   0.46    0.46    0.15   0.1

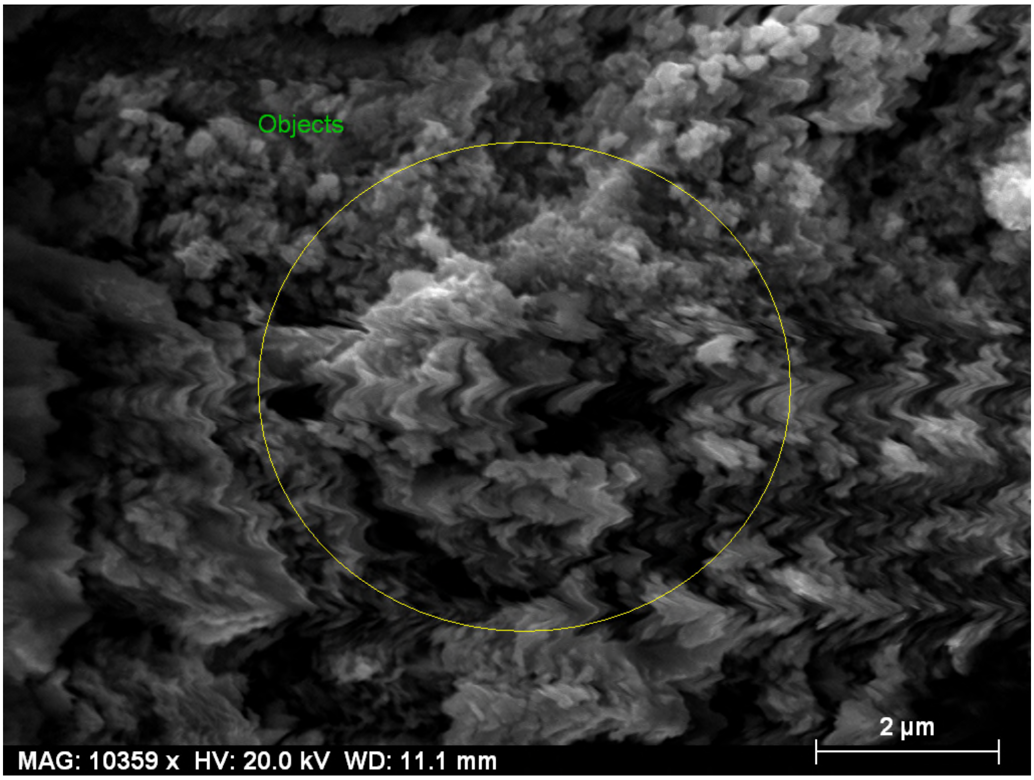
Phosphorus K-series   0.53    0.53    0.30   0.0
```





Spectrum: Objects

```
Element     Series   unn. C norm. C Atom. C Error
                     [wt.%]  [wt.%]  [at.%]   [%]
-------------------------------------------------
Oxygen     K-series  70.42   70.42   78.51  22.4
Iron       K-series  16.02   16.02    5.12   0.5
Carbon     K-series   9.60    9.60   14.26   3.7
Silicon    K-series   1.44    1.44    0.92   0.1
Calcium    K-series   1.98    1.98    0.88   0.1
Phosphorus K-series   0.54    0.54    0.31   0.0
-------------------------------------------------
```


Objects
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Spectrum: Objects


Element      Series   unn. C norm. C Atom. C Error
                      [wt.%]  [wt.%]  [at.%]   [%]
--------------------------------------------------
Iron        K-series  45.68   76.32   54.60    1.3
Silicon     K-series   1.41    2.35    3.35    0.1
Oxygen      K-series   4.59    7.67   19.16    1.1
Calcium     K-series   3.95    6.61    6.59    0.2
Carbon      K-series   1.97    3.30   10.96    0.6
Manganese   K-series   0.95    1.59    1.16    0.1
Sodium      K-series   0.02    0.03    0.06    0.0
```

Appendix VIII Phosphate adsorption kinetics

The kinetic data obtained were fitted by means of different models.

Data fitting to Pseudo-second order kinetic model

Kinetic data can be described by means of pseudo-first (Ho and McKay 1998), or pseudo-second order models. A pseudo-second order model assumes that chemisorption is the rate determining step in the adsorption process. From the pseudo-second order model the initial adsorption rate can also be obtained (Ho 2006). This is an additional advantage of the pseudo-second order equation over the pseudo-first order equation.

The pseudo-second order kinetic rate equation is expressed as:

EQUATION 0-1

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

Where q_e and q_t are the sorption capacity at equilibrium and time t, respectively (mg g^{-1}) and k_2 is the rate constant of pseudo-second order sorption (g $mg^{-1}min^{-1}$).

For the boundary conditions t = 0 and t = t and q_t = 0 to q_t = q_t, the integrated form of Equation 0-1 becomes:

EQUATION 0-2

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$$

Equation 0-2 can be rearranged and linearized to obtain:

EQUATION 0-3

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Equation 0-3 can be re-written as:

EQUATION 0-4

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

Where h can be regarded as the initial sorption rate as q_t/t approaches zero (Ho and McKay 1999).

If a pseudo-second order model is applicable to the kinetic data, the plot of t/q_t against t should result in a linear relationship, from which the rate constant (k_2), equilibrium adsorption capacity (q_e) and initial rate of sorption (h) can be determined.

Figure 17 presents the plot of t/q_t against t for the adsorption of orthophosphate on the three types of GIH-pellets and Ferrosorp Plus. It can be seen that the straight lines fit well for the experimental data. Table 32 presents the regression coefficients for the linear plots (R^2). The closer the R^2 value approaches 1, the better the equation describes the experimental data. It can be observed (Table 32) that in all the cases R^2 was ≥ 0.990, representing a good fit. Since the pseudo-second order equation is based on the assumption of chemisorption {;Ho, 1999 #553}, it can be concluded that the data obtained may indicate chemisorption was involved in the sorption of orthophosphate on the GIH-pellets and Ferrosorp Plus. Chemisorption typically shows bonding energies of above 200 kJ/mol (Sperlich 2010). In chemisorption the solute reacts with the surface either to form an ionic bond or a covalent bond. However, we don’t have sufficient data to conclude chemisorption really is involved here.

In Table 32 the calculated pseudo-second order model parameters are presented. These parameters are determined from the slope and intercept of the straight lines presented in Figure 41. It can be observed that the GIH-pellets produced from Huijbergen residual show highest q_e and h, and the GIH-pellets produced from the old Spannenburg residual show the lowest q_e and h among the tested adsorbents. As mentioned before, this may correlate with the specific surface area and iron content of the materials (see chapter 4). The GIH pellets produced from the fresh Spannenburg residual show slightly higher q_e and h compared to Ferrosorp Plus, however the order of magnitude is similar. Although the iron content of both these materials is in a similar range, their specific surface area is significantly different. Specific surface area of Ferrosorp Plus was higher. This indicates that iron content is a more important parameter than specific surface area in the adsorption process.

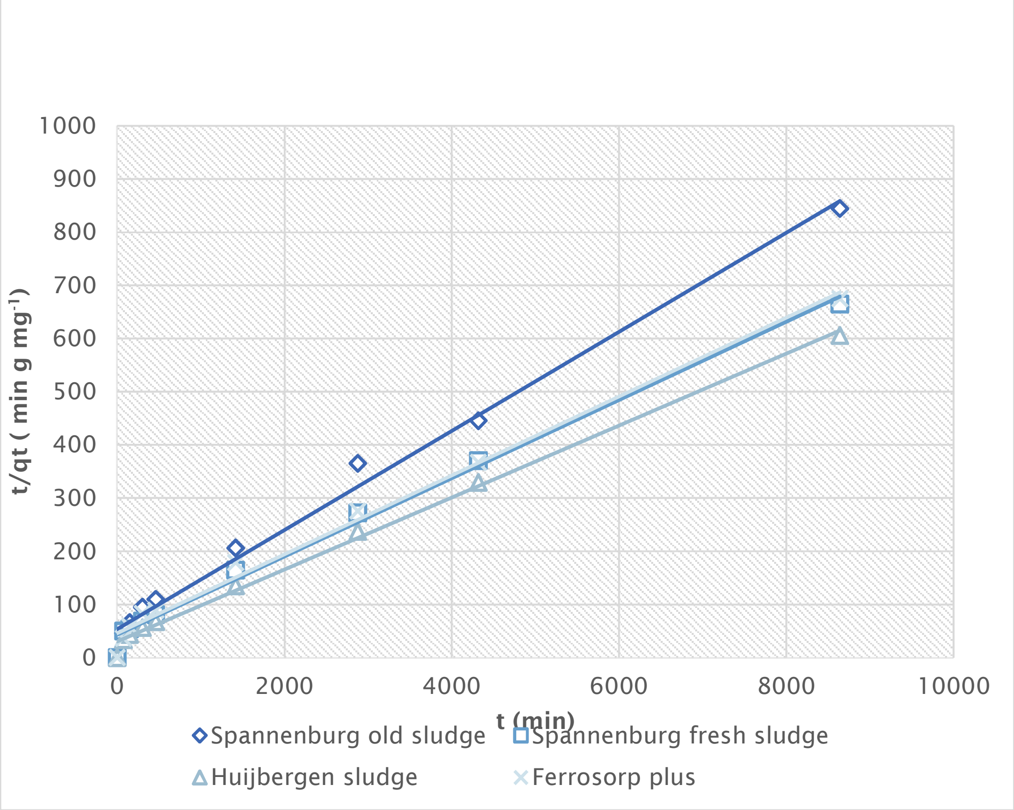


FIGURE 41 PLOT OF t/q$_t$ AGAINST t. APPLICATION OF PSEUDO-SECOND ORDER KINETIC MODEL TO THE EXPERIMENTAL DATA OF FIGURE 5-1.

TABLE 32 PSEUDO-SECOND ORDER KINETIC PARAMETERS FOR THE ADSORPTION OF ORTHO-PO$_4$ BY GIH PELLETS AND FERROSORP PLUS. R^2 IS THE CORRELATION COEFFICIENT. q$_e$ IS EQUILIBRIUM ADSORPTION CAPACITY. k$_2$ IS PSEUDO-SECOND ORDER RATE CONSTANT. h IS INITIAL SORPTION RATE.

Adsorbent	**Pseudo-second order kinetic parameters**			
	R^2	**q_e (mg g^{-1})**	**k_2 (g mg^{-1} min^{-1})**	**h (mg g^{-1} min^{-1})**
Spannenburg old residual	0.990	10.7	0.0002	0.019
Spannenburg fresh residual	0.992	13.6	0.0001	0.024
Huijbergen residual	0.996	14.8	0.0002	0.033
Ferrosorp plus	0.990	13.5	0.0001	0.022

Data fitting to intra-particle diffusion model

Adsorption in porous media is a sequential process consisting of four phases, including bulk transport of the solute to the boundary layer that surrounds the adsorbent particle (external transport), transport of the solute mass to the surface of the adsorbent through the boundary layer (external transport), transport through pores within the adsorbent via a combination of pore diffusion and surface diffusion mechanisms (internal transport) and adsorption of the solute to the surface (reaction). According to Thomson et al. (Thomson, Aragon et al. 2005) the bulk transport and adsorption on the adsorbent surface is often not rate limiting. In general the transport mechanism of main concern will be the external film diffusion and intra-particle diffusion. Therefore, the possibility of intra-particle diffusion was investigated by fitting the kinetic data to the intra-particle diffusion model of Weber and Morris (Weber and Morris 1963).

The intra-particle diffusion equation is:

EQUATION 0-5

$$q_t = k_i t^{0.5}$$

where q_t is the sorption capacity at time t and k_i is the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$).

The plot of adsorption capacity (q_t) at time t against square root of time ($t^{0.5}$) should be linear if intra-particle diffusion is involved in the sorption process (Ho, Ng et al. 2000). Figure 42 presents the plot of q_t against $t^{0.5}$ based on the kinetic data. It can be observed in Figure 42 that the curves are steeper in the beginning and tend to pass through the origin. At later phase, the slope of the curves decreases and they deviate from the origin. The first straight portion depicts macro- and meso-pore diffusion and the second one indicates micro-pore diffusion. Extrapolation of the linear portions of the plots back to the y-axis gives the intercepts, which provide the measure of the boundary layer thickness. The deviation of straight lines from the origin may be due to difference in rate of mass transfer in the initial and final stages of adsorption. Furthermore, such deviation of straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step.

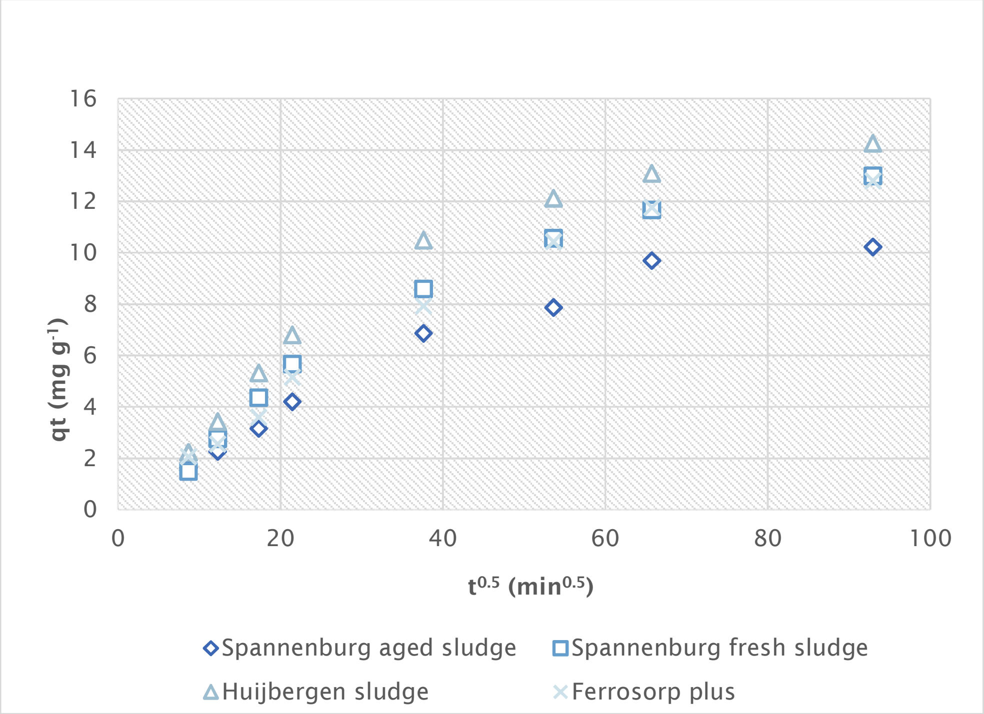


FIGURE 42 PLOT OF q_t AGAINST $t^{0.5}$. APPLICATION OF INTRA-PARTICLE DIFFUSION MODEL TO THE EXPERIMENTAL DATA OF FIGURE 5-1.

Appendix IX Arsenic adsorption kinetics

Pseudo-second order kinetic model

A pseudo-second order model is used to evaluate the experimental data from adsorption kinetics. This model has been described in the chapter of laboratory scale orthophosphate adsorption experiments. Figure 43 presents the plot of t/q_t against t for the adsorption of As on three types of GIH-and Ferrosorp Plus. It can be seen that the straight lines fit well for the experimental data. The correlation coefficients for the linear plots (R^2) have been listed in Table 33. The closer the R^2 value approaches unity, the better the equation describes the experimental data. It is evident that in all the cases pseudo-second order model described the data well. The pseudo-second order equation is based on the assumption chemisorption takes place {Ho, 1999 #553}, and thus it may be concluded that the data on the adsorption of As on the GIH-pellets and Ferrosorp Plus may indicate chemisorption being involved.

In Table 33 the pseudo-second order parameters are presented. These parameters are determined from the slope and intercept of the straight lines presented in Figure 43. It can be observed that the GIH-pellets produced from Huijbergen residual showed highest q_e and h and the GIH-pellets produced from old Spannenburg sludge showed the lowest q_e and h among the tested sorbents. This observation is in-line with the results of laboratory scale orthophosphate adsorption experiments discussed in chapter 5, however there is a clear difference in terms of the magnitude of kinetic parameters. This was due to the fact that a much higher concentration of orthophosphate per gram of adsorbent was applied in adsorption experiments (10.4 mg/g to 52 mg/g) compared to As adsorption experiments (1 mg/g to 0.07 mg/g).

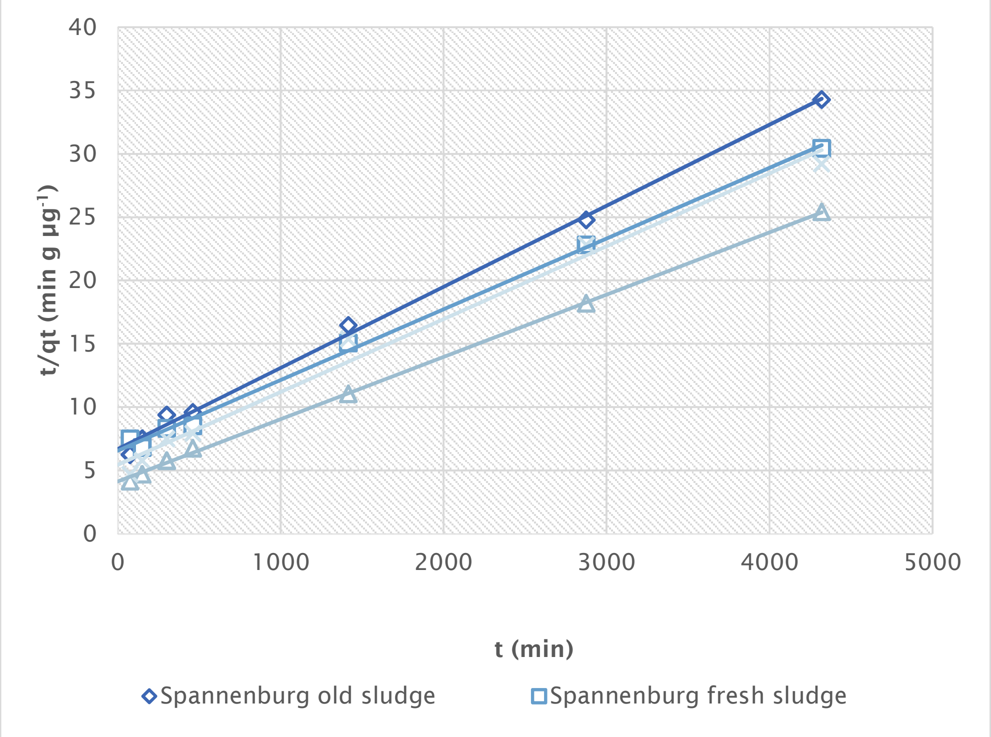


FIGURE 43 PLOT OF t/q_t AGAINST t. APPLICATION OF PSEUDO-SECOND ORDER KINETIC MODEL TO THE EXPERIMENTAL DATA OF FIGURE 7-1

TABLE 33 PSEUDO-SECOND ORDER KINETIC PARAMETERS FOR THE ADSORPTION OF As BY GIH-PELLETS AND FERROSORP PLUS. R^2 IS THE CO-EFFICIENT OF DETERMINATION. q_e IS EQUILIBRIUM ADSORPTION CAPACITY. K_2 IS PSEUDO-SECOND ORDER RATE CONSTANT. H IS INITIAL SORPTION RATE.

Adsorbent	**Pseudo-second order kinetic parameters**			
	R^2	**q_e (µg g^{-1})**	**k_2 (g µg^{-1} min^{-1})**	**h (µg g^{-1} min^{-1})**
Spannenburg old residual	0.997	153.6	6.1×10^{-6}	0.149
Spannenburg fresh residual	0.997	178.6	4.8×10^{-6}	0.153
Huijbergen residual	0.999	204.1	5.8×10^{-6}	0.243
Ferrosorp plus	0.987	172.4	6.2×10^{-6}	0.184

Intra-particle diffusion model

The possibility of intra-particle diffusion was investigated by fitting the kinetic data to the intra-particle diffusion model of Weber and Morris (Weber and Morris 1963). The intra-particle diffusion equation is described in chapter 5. The plot of adsorption capacity (q_t) at time t against square root of time ($t^{0.5}$) should be linear if intra-particle diffusion is involved in the sorption process (Ho, Ng et al. 2000). Figure 44 presents the plot of q_t against $t^{0.5}$ based on the kinetic data of As sorption on GIH-pellets and Ferrosorp Plus, and Table 34 presents the correlation coefficient (R^2) and intra-particle diffusion model parameters determined from the straight lines. It can be observed that the R^2 values are close to unity. Moreover, the straight lines show (almost) no intercept on the vertical axis, showing intra-particle diffusion to be the main rate controlling mechanism.

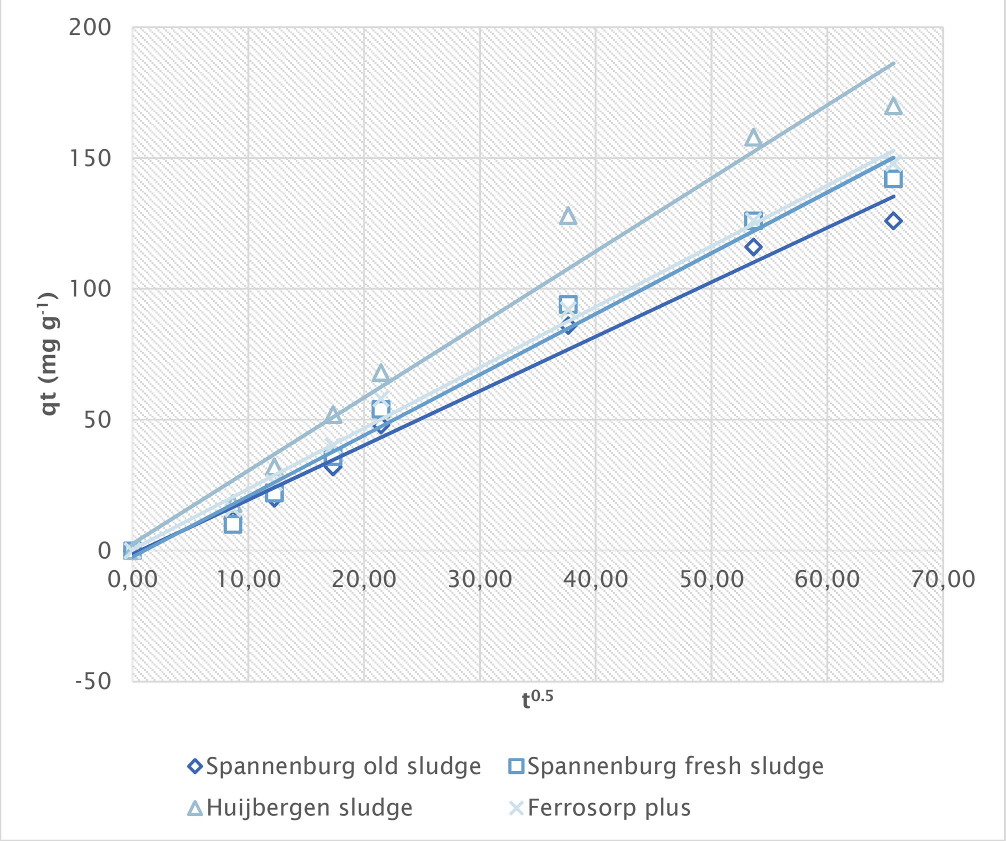
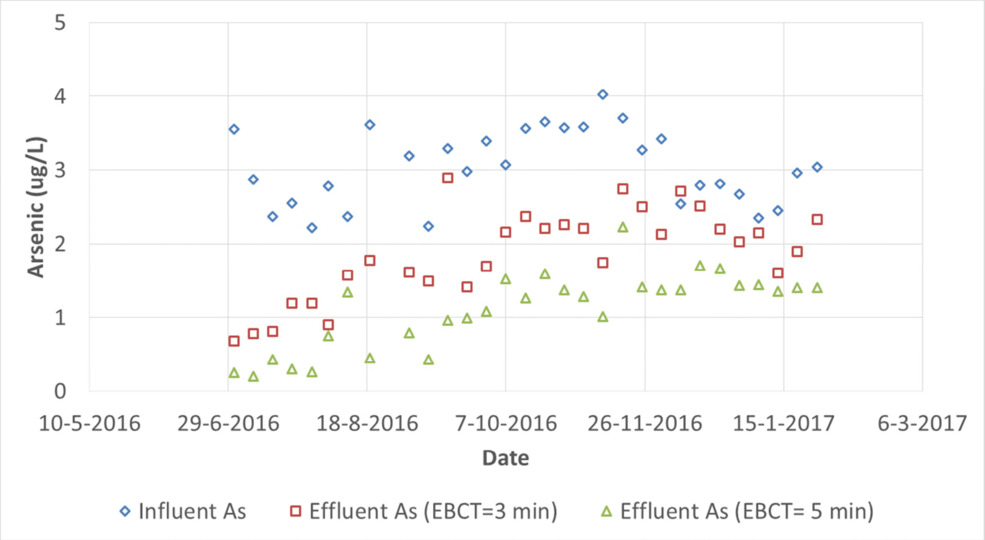


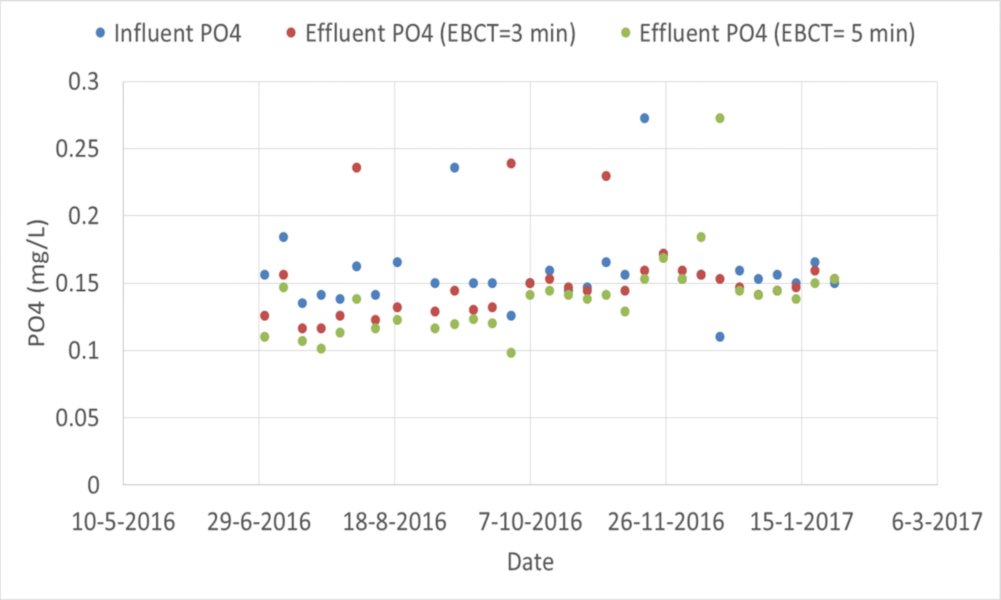
FIGURE 44 PLOT OF q_t AGAINST $t^{0.5}$. APPLICATION OF INTRA-PARTICLE DIFFUSION MODEL TO THE EXPERIMENTAL DATA OF FIGURE 7-1.

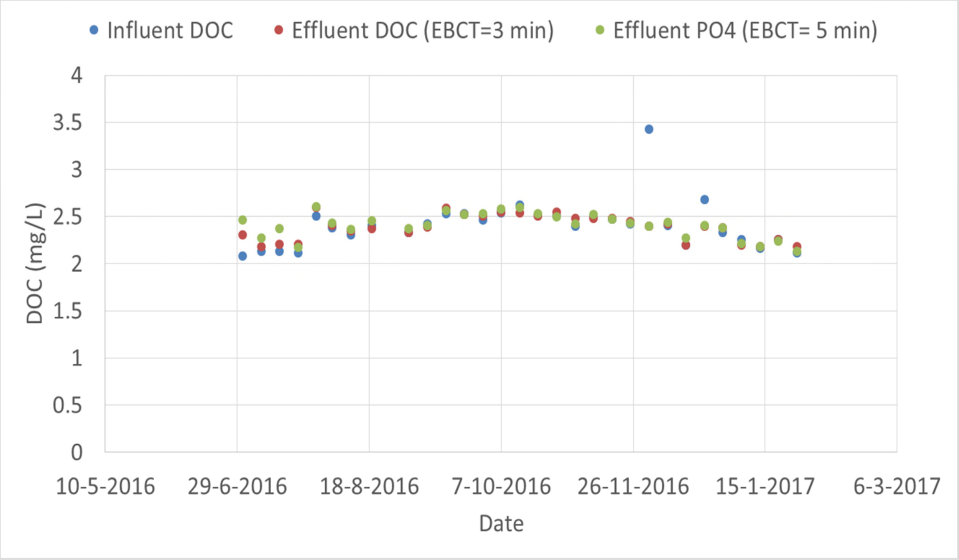
TABLE 34 INTRA-PARTICLE DIFFUSION MODEL PARAMETERS FOR THE ADSORPTION OF As BY GIH PELLETS AND FERROSORP PLUS. R^2 IS THE CO-EFFICIENT OF DETERMINATION. K_i IS INTRA-PARTICLE DIFFUSION RATE CONSTANT. I IS Y-INTERCEPT OF THE STRAIGHT LINE.

Adsorbent	**Intra-particle diffusion model parameters**		
	R^2	**K_i (µg g^{-1} $min^{-0.5}$)**	**I (µg^{-1})**
Spannenburg old residual	0.983	2.08	-1.32
Spannenburg fresh residual	0.986	2.32	-2.37
Huijbergen residual	0.972	2.79	2.61
Ferrosorp plus	0.993	2.32	0.53

Appendix X GIH effluent quality at Katwijk



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3
2.5
2
1.5
1
0.5
0
10-5-2016
29-6-2016
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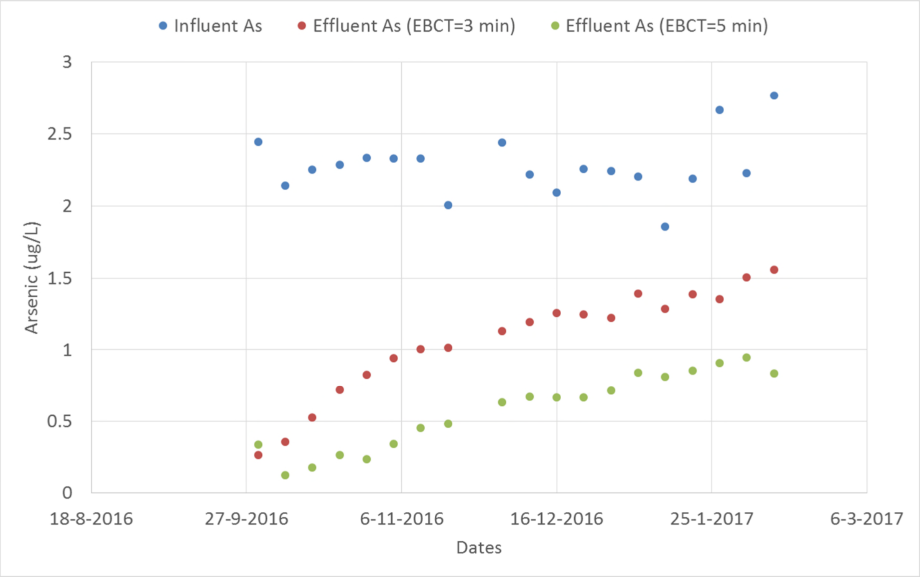
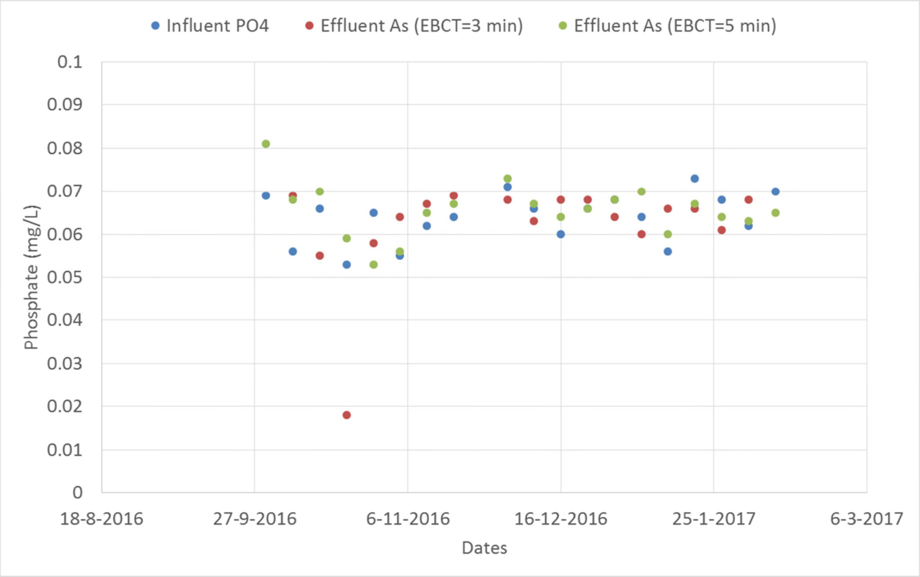
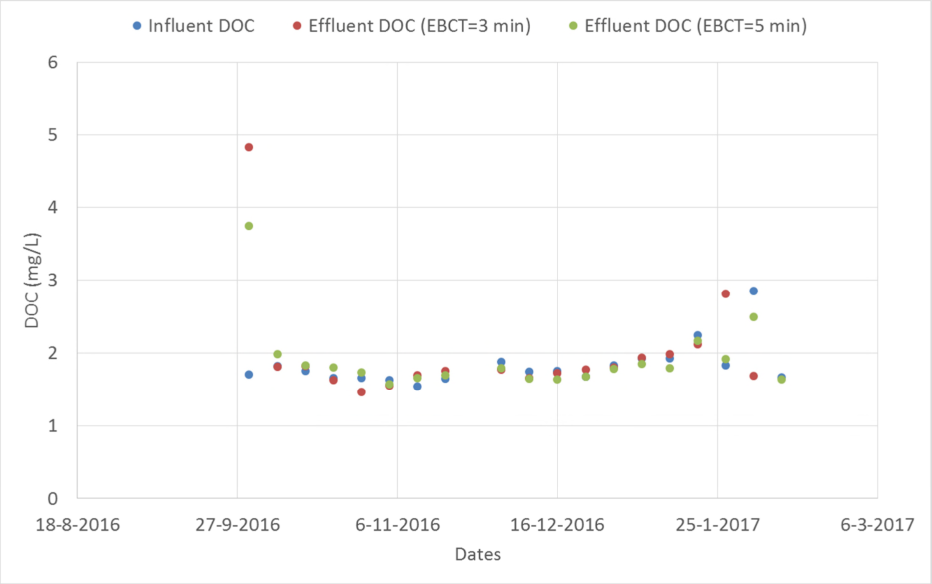
15-1-2017
6-3-2017
Date

Appendix XI GIH effluent quality at Prinsenbosch



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● Effluent DOC (EBCT=3 min)
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1
2
3
4
5
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6-3-2017
Dates