production of uniform akaganeite (β–FeOOH) crystals by hydrolysis

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Summary

This report deals with the production of monodisperse β-FeOOH fibres by hydrolysis. The aim of the work was to obtain monodisperse fibres for inhalation experiments in a lung model. After a short introduction on crystallography, the formation of β-FeOOH or akaganeite is presented. The reaction steps that lead to the growth of akaganeite are presented as far as they are known. The elongated growth shape of akaganeite is explained from crystallographic theory, and some hypotheses on the presence of twins and the promotion of large and uniform crystals are given.

The crystals were made by maintaining an aqueous solution of 0.01-1.0 M $FeCl_3$ and 0.0-0.1 M HCl at 65 or 100 °C in a thermostated oven. Crystals were also made by slowly adding water to an $FeCl_3$/HCl solution. Hematite was obtained sometimes, either alone or in combination with akaganeite. The crystals were viewed using a transmission electron microscope and were analysed by X-ray diffraction, electron diffraction and elemental analysis. The Fe^{3+}-concentration and pH of the solutions were measured.

Crystals of the uniform productions varied in length between 0.2 and 1.2 μ. The relative standard deviation of the long crystals was around 10 % in length, diameter and aspect ratio, when twins were eliminated. That production gave a yield of 0.01 grams or circa 10^{11} crystals. The aspect ratio of the uniform productions was circa 5. Higher aspect ratios could be obtained as well, but then crystals were less uniform, both length and diameter varying by a factor two.

At 65 °C only cigar shapes of aspect ratio 4 to 5 were obtained, while at 100 °C needles of aspect ratio between 4 and 40 were made.

Silicon, which hinders the growth of akaganeite, was present in all crystals. Silicon concentration varied from 1.2 to 35 atomic percent, averaging about 6 atomic percent. Its origin could not be traced. Presence of silicon in the laboratory air is the most probable of all suggestions on the origin of akaganeite. Exclusion of silicon may lead to larger crystals.

The size of the crystals is increased by starting at a low pH, uniformity is increased by starting at a low ferric ion concentration, and the presence of twins is increased by increasing the HCl-concentration.

As the reproducibility of the experimental results is moderate, it is hardly possible to make identical crystals in different production runs.

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Chapter 1: Introduction

This is the report of half a year of experimental work, being the last part of the study of chemical engineering of the Department of Chemical Technology at the Delft University of Technology. The experimental work is performed for a project on fibres and their behaviour in human lungs. The project is in the hands of professor Dr. B.H. Bibo, Dr. Ir. J.M. Marijnissen, Dr. Ir. S.M. Lemkowitz and Drs. J.R.F. Buwalda. Acknowlegdements are due to them and to C.D. de Haan for the hours he spent with me at the transmission electron microscope and to Dr. R.A. Kuhnel for his helpful suggestions on crystal theory and practice. The aim of the project as a whole is to make uniform fibres, disperse them in a lung model and detect the behavior and deposition site of the fibres. The aim of the project is to learn about fibre behaviour and possible damage in human lungs.

My experimental work constitutes only a small part of this project. In half a year, my aim was to make one or two types of uniform respirable fibres. An idea of how these fibres could be made was already present. A literature study by M. van Pinxteren reported the possiblity to make uniform fibres by crystallization. Information from R.A. Kuhnel resulted in the choice for crystallization by slow hydrolysis of ferric solutions. A search for an experimental procedure that results in uniform ferric oxide fibres led towards a publication by E. Matijevic [mat78]. In this publication, an experimental set-up was given that gave rather uniform β-FeOOH fibres with length of 0.25 μ and diameter of 0.025 μ.

The goal of the work was to produce fibres. The experiments started when no theory was known at all. During the experimental period, literature was searched that explained the growth mechanism of akaganeite, and an explanation was sought for the elongated growth shape of the crystals. The literature found on both subjects was sufficient for its use. During the experiments, not much was known about akaganeite and its formation.

Experimental continuation was based on experimental results only and not on theoretical expectations. Only at the end of the experimental period, theories were sought that would explain characteristics of the growth of akaganeite, and some final experiments were carried out to check their validity.

The incompleteness of theory is partly caused by our main interest for practical results and partly by the fact that theory concerning crystallization by hydrolysis is only partly known. On the mechanism of formation, many publications from the period 1965-1975 have been read. In these publications only suggestions for the first step of the formation are presented. Conclusions on the exact mechanism are not made, neither for hydrolysis, nor for the following steps. Literature on industrial crystallization and crystal growth, dealing with influencing size, shape, yield and other crystal growth factors, does not pay attention to crystallization by hydrolysis, although crystallization by hydrolysis differs from normal crystallization from solutions.

The theories developed to explain the characteristics of the experiments are usually based on few experiments. Conclusions that are drawn from the experiments are valid for the experiments themselves, but as too little theory and too few experiments are known, no validity outside the experiments performed may be expected.

This report is organized as follows:
Chapter 2 describes the theory concerning this report. The chapter starts with a short introduction on crystallography. The second part of this chapter contains the features, formation process and growth shape of akaganeite. The chapter ends with a discussion on the definition, promotion and way of determination of monodispersity.

In chapter 3 the experimental procedures and analysis methods are presented.

Chapter 4 contains the experimental results. Observations made during the experiments are reported and results of the analyses are presented on the basis of methods used.

These results are discussed in chapter 5. Quantities like reproducibility, monodispersity, shape and size are discussed and compared with theory where possible. The results are also compared with the results obtained by Matijevic.

The last chapter concludes upon the best way to make monodisperse akaganeite fibres and gives suggestions for further research.

The report ends with an epilogue for the use of the leaders of the project, and a literature list. The illustrations are presented in a seperate booklet, together with a more detailed description of the experiments.

Chapter 2: Theory

As stated in the introduction, far too little theory is found to explain all characteristics of the experimental results. Some theory is known on the formation of akaganeite is known. On growth conditions or influencing the growth in order to make crystals in a desired shape or size, no theory was available. The general crystal growth theories are known, but insight in which factors would be of interest was not present at all. The main part of that theory has originated from results that needed explanation. The first things that needed explanation were why the crystals grew, what their mechanism of formation was, and why they were growing in an elongated shape. Both these questions are answered in this chapter. The rest of the theories in this chapter are found or deduced later.

This chapter starts with a short survey on crystallography. This survey is presented because crystallography is the basis of crystal shape and growth. It is easier to understand processes that occur when growing akaganeite when some crystallographical knowledge is present. After this introduction, the structure and formation of akaganeite are handled. The chapter ends with a short discussion on monodisperity.

2.1 Crystallography

A definition of a crystal as it is accepted nowadays is: a crystal is a homogeneous, anisotropic discontinuum. Homogeneous says a crystal has an constant composition throughout the crystal, anisotropic says the crystal contains different properties in different directions and discontinuum says the crystal consists of atoms and free space between the atoms.

Crystallography is the study of crystals and of the principles that define internal and external shape and growth. The external shape is called habit of a crystal. The repeating structure is called a lattice. The repeating structure is a primitive cell. The size and shape of the primitive cell determine the crystal system. The six basic crystal systems are shown in figure 1. The contents of a cell can be different for each kind of crystal, the combination of cell content and shape are unique for each type of crystal. Akaganeite for instance has a tetragonal unit cell; a_1 and a_2 are 3.030 Å and c is 10.535 Å [jcpds]. The content of the cell is shown in figure 2 [mac60]. Some primitive cells can be multiplied to give cells of higher symmetry. Those are called unit cells. Primitive cells are unit cells as well. There is a total number of fourteen different unit cells [kle85].

Unit cell type is one of the habit-determining factors, it can be seen as the genetic information of a crystal. Habit is also influenced by the environment at the time of growth. Environment includes all influencing factors, like aggregation state (melt, solution, gasphase), temperature, pressure, available free space, concentration of solution, direction of movement and speed of solution, presence of contaminations, etcetera [che84].

Due to the repetitive structure, points in a crystal can be descibed with co-ordinates. A unit cell has co-ordinates like (0,0,0), (1,0,0), (1,1,0), and may also have a lattice point or node at (1/2,0,0) for instance. The origin can be chosen freely along the lattice. A, b and c are the axes of the crystal co-ordinate system.

Planes, built up of nodes, play a mayor role in the habit of a crystal and are named with indices. The most common way of naming is giving Miller-indices (hkl) to each plane. Miller-indices are the integer inverse values of the cut-of distances of the plane on the a, b and c axes. So a plane intercepting at $(1,0,0)$, $(0,1,0)$ and $(0,0,\infty)$ has Miller indices (110). Note the absence of commas, to distinguish co-ordinates and Miller indices. Miller indices can have negative values, indicated by a dash above the digit. Planes are indexed within a unit cell. Identical planes in different unit cells have the same Miller indices, as the origin can be chosen anywhere.

2.2 Structure and formation of akaganeite

The mineral akaganeite was discovered in the Akagané-mine in Japan in 1961 [mac62]. Before discovery in nature the material, β-FeOOH had already been synthesized. Various methods are described by Mackay [mac60]. The material is spindle-shaped and has a length of circa 0.5 μ. Star- and X-shapes are also found. The natural akaganeite contains no chloride, but it contains 3.5 % SiO_2 and 1.3 % Al_2O_3 [mac62].

2.2.1 Crystal structure

The crystal structure of akaganeite is that of hollandite (α-MnO_2) and is depicted in figure 2 [mac60]. The unit cell contains 8 FeOOH-units and two units of Cl^- or H_2O. The correct structure formula is therefore $Fe_8(O,OH)_{16}(Cl,F,H_2O)_2$ instead of FeOOH [mac60].

The Fe^{3+} ions are surrounded octahedrally by six O^{2-}/OH^- ions. The body-centered-cubic positions are occupied by Cl^- or H_2O. Synthetic β-FeOOH always contains chlorine [mac62]. Initial Cl content is 1/4.79 (Cl/Fe-atomic ratio), but it can be lowered by repeated washing to Cl/Fe < 1/45. Normally, between 2 and 4 percent chlorine is found [mac60].

The crystals are elongated along the [001]-axis. Twinning, resulting in hexagonal stars or X-shapes, occurs, the twin plane is (332) [mac60]. Heating of a single crystal in the electron microscope beam may transform the crystal, giving streaks perpendicular to [001] [mac60]. Prolonged heating in air results in α-Fe_2O_3 (hematite) [mac60].

No explanation was found on the occurence of twinned crystal, apart from a short notice of Mackay [mac60]. He defines a pseudo-unit cell with edges a/3 and c, based on a body-centered-cubic cell of oxygen and iron. Twin plane then is (112), which is the usual twin plane in α-iron and α-tungsten materials. Kuhnel proposes a theory in which there is a lack of free water to hydrolyse Fe^{3+} ions. If such a deficiency arises after some polymerisation has taken place, a plane containing many water molecules will be shared, and will be the basis of the star-shaped crystals.

2.2.2 Formation of akaganeite

Akaganeite is usually formed by hydrolysis of Fe^{3+} solutions, though it can also be prepared by damp oxidation of $FeCl_2.4H_2O$, by dry oxidation of $3Fe(OH)_2.FeCl_2$ and by some other processes [mac60]. Hydrolysis can occur at room temperature, the process is slower the lower the pH. Hydrolysis can be promoted by adding a base, by heating in the absence or presence of a base and by adding an oxidising agent followed by base addition or heating [mat78]. Temperature is a factor that advances hydrolysis. This is easily seen because the colour of the suspension changes to yellow and brown when the temperature increases. This process is partly reversible: on cooling down the colour fades and conductivity decreases [mat66].

The exact process steps from Fe^{3+} to akaganeite are not found in literature. For the first step, hydrolysis, several suggestions have been given, such as:

$$Fe(H_2O)_6^{3+} + H_2O \rightarrow Fe(H_2O)_5OH^{2+} + H_3O^+ \tag{1}$$

$$Fe(H_2O)_5OH^{2+} + H_2O \rightarrow Fe(H_2O)_4(OH)_2^+ + H_3O^+ \tag{2}$$

$$2\ Fe(H_2O)_6^{3+} \rightarrow (H_2O)_4\text{-}Fe\text{-}(OH)_2\text{-}Fe\text{-}(H_2O)_4 + 2\ H_3O^+ \tag{3}$$

This last compound is linked to form octahedra. Mackay [mac62]

A mixture of the following ferric ion complexes is present in the solution:

$Fe(H_2O)_6^{3+}$ / $Fe(H_2O)_5OH^{2+}$ / $Fe_2(H_2O)_8(OH)_2^{4+}$ / $Fe(H_2O)_4(OH)_2^+$

Feitknecht [fei62]

The precipitation process (of hematite and goethite, α-FeOOH) concerns hydrolysis of $Fe(H_2O)_6^{3+}$, which is promoted by heating, by increasing pH on dilution or by addition of OH^--ions or other reagents to remove H^+-ions. Hydrolysis proceeds by progressive elimination of H^+ from $Fe(H_2O)_6^{3+}$, followed by formation of polymeric species with oxo- and hydroxo linkages. After extended periods of ageing, crystalline products may be detected.

Atkinson [atk68]

$Fe^{3+} \leftrightarrow FeOH^{2+} + H^+$ (4)

$FeOH^{2+} \leftrightarrow Fe(OH)_2^+ + H^+$ (5)

$2\ FeOH^{2+} \leftrightarrow Fe_2(OH)_2^{4+}$ (6)

On continued hydrolysis, particularly at higher Fe concentrations, higher molecular weigth species are doubtless formed by stepwise condensation of the simple hydrolysis products. There is evidence for the existance of $Fe_3(OH)_4^{5+}$, and $[Fe_4O_3(OH)_5]NO_3$ has been isolated as well. Spiro has identified material with the approximate composition $[Fe_4O_3(OH)_4(NO_3)_2(H_2O)_{1\cdot5}]_{250}$. Knight [kni74]

The line in the literature is: hydrolysis takes place, it stops before $Fe(OH)_3$ is formed. The following step is condensation polymerisation of simple hydrolysis products. The resulting material is colloidal or gelatinous. This material slowly transforms to the akaganeite crystals.
As the formation of FeOOH from $Fe(H_2O)_6^{3+}$ causes a net release of three protons, the reaction enhancing effects of pH increase are obvious. The promotion of reaction by higher temperatures may be caused by increased dissociation of H_2O in OH^- and H^+, which increases OH^-/H^+-ratio and thus pH.

The reason for formation of β-FeOOH instead of for instance α-Fe_2O_3 is not clear, though it is known that prolonged heating or different concentrations gives α-Fe_2O_3 instead of β-FeOOH [mat78]. It seems akaganeite only grows when hydrolysis can not continue to give crystals like hematite or other iron oxides. For instance, $Fe(OH)_3$ will arise when hydrolysis is fast and complete. To prevent formation of $Fe(OH)_3$ in solutions where Fe-ions are present, a pH under circa 2.0 has to be maintained.

Silicon is included in the crystals that were made. Theories that account for the inclusion of silicon in the crystals and its presence on the outside of the crystals have not been found. In the literature on synthetic akaganeite, the presence of silicon is not mentioned. However, silicon is known to show an inhibiting effect on the growth of several crystals, amongst which are goethite and manganese oxides [kuh75]. The fact that silicon is mainly found on the outside of the crystals could mean that inclusion of silicon is a very slow process compared to the growth of akaganeite. Silicon would then concentrate in the outside layer when ferric is no longer causing growth. Another reason can be that inclusion of silicon inhibits or largely hinders further growth of crystals, as is suggested above.

Due to the hydrolysis process, crystal formation occurs differently from the usual crystallization processes. Normally, crystallization occurs upon cooling a saturated solution or concentrating a saturated solution. Here however, diluting or heating are the main methods. This can be understood when it is realised that one of the reactants is water, which acts as a proton-acceptor. The capacity of water to accept a proton increase as the H_3O^+/OH^--ratio decreases. Therefore dilution gives a higher concentration of proton acceptors and is a kind of supersaturation.

This situation makes the usual theories on crystal growth not readily applicable to growth of akaganeite. Theory on for instance crystal size states that the size of crystals can be enlarged by creating a low rate of nucleation. A low rate of nucleation can be achieved by lowering the supersaturation.

Lowering the supersaturation, however, is not an unambiguous process on hydrolysis. When adding water, one of the reactants is concentrated and one is diluted. The same goes for adding $FeCl_3$. The effect of either change is therefore to be discovered only by experiment.

2.2.3 Growth shape

The growth shape of akaganeite is distinctly non-uniform. The reason why akaganeite grows in the shape of needles is of interest. Knowing the reason may facilitate growing akaganeite crystals, and it may also illustrate how other needle-shaped crystals can be formed. An explanation for the growth shape or habit of akaganeite is thus been sought and is presented here.

The crystal habit, when it is based only on the 'genetic' information (see page 8), is called the equilibrium growth shape of a crystal. The elongated form of akaganeite must have its basis in crystal structure and not in the environment, as the elongated form is present in all known akaganeite samples.

Crystals with non-uniform equilibrium shape must have different growth rates in different directions [che84]. Planes with low growth rates are the planes forming the habit of a crystal. This principle is shown in figure 3.

Several theories are proposed that account for the equilibrium shape of a crystal.

The first simple theory is from Bravais saying: Low growth rates are characteristic for sides with (hkl) orientation, parallel to atomic nets with largest distance d_{hkl}. As d_{hkl} is proportional with $(h^2+k^2+l^2)^{-1/2}$, sides with low indices grow slowest.

The Bravais-theory does explain why (100) is found more often in the habit than for instance (314) or (251), but it does not explain the advantage of (001) over (100) and (010). Or rather, it does not explain when $(h^2+k^2+l^2)^{-1/2}$ is used instead of the real plane distances.

More recently Donnay and Harker have refined the Bravais theory. They correct for certain symmetry effects not included by Bravais. Apart from that, at their time X-ray crystallography was sufficiently developed to obtain the real atomic distances between planes in Å. The fact that real atomic distances in Å have to be used instead of $(h^2+k^2+l^2)^{-1/2}$ was found out from an example by Hottenhuis [hot88]. The d_{hkl}-values used are the values as they are obtained by X-ray crystallography. D_{hkl}-values of different planes are given for many crystals in the JCPDS-cards [jcpds]. For akaganeite, JCPDS 34-1266 gives as highest d_{hkl}-value 7.467 Å for the (110)-plane, while (211), the first plane in c-direction, is sixth, with d_{hkl}= 2.55 Å (table 4). As the plane growth rates are proportional to the reciprocals of the d_{hkl}-values, a habit as shown in figure 5 will grow. This shape is in accordance with the known growth shape of akaganeite.

2.3 Monodispersity of the crystals

Monodispersity of the fibres is desired because the evaluation of fibre behaviour in the lung is increadibly complex when a distribution of fibres is inhaled. Determination of monodisperity is not as simple as it seems. In the first place, the definition of monodispersity is not straightforward. Besides, for a fibre, different parameters may be used for measuring the monodispersity of a sample.

Monodispersity of a quantity is often accepted when the geometrical standard deviation of that quantity does not exceed 1.2. Geometrical standard deviation represents x_{84}/x_{50}. Sometimes a limit of 1.1 is found, which is of course much more monodisperse. Therefore, a geometrical standard deviation of 1.1 is to be strived for.

When more or less monodisperse materials are considered, geometrical standard deviation minus one approximates the relative standard deviation. The standard deviation represents $x_{84}-x_{50}$, the relative standard deviation thus represents x_{84}/x_{50} -1. Thus the relative standard deviation can also be used for determination of monodispersity.

Another problem is to choose the relevant parameter when checking for monodispersity. Fibrous material has several parameters, like length, aspect ratio, and volume, which may well differ in monodispersity. As no standard has been defined for fibres, the best is to compare several parameters like length, diameter, surface or volume. In this report, length, breath, aspect ratio and projected surface area are considered. Monodispersity is calculated with the relative standard deviation of the population.

Achievement of monodispersity when growing crystals can be promoted by creating a very short period of nucleation and a long period of growth, during which no new nuclei can develop, or by seeding a solution with rather uniform seeds and growing the crystals while no new nuclei can arise, or by momentary crystallization of all material. The last method is practically impossible. The first two methods are similar. Their main characteristic is that no nucleation can take place during growth. Preventing the development of nuclei is possible by creating low supersaturations. The two factors that may cause a low supersaturation are low ferric ion concentration and low pH.

Chapter 3: Experiments

As already mentioned, the experimental methods are based on a publication by Matijevic [mat78]. Matijevic made different crystals from several starting solutions. When using $FeCl_3$ as a starting solution, apprropiate conditions resulted in formation of needle-shaped β-FeOOH. Basically these conditions were a temperature of 100 °C maintained during 24 hours, of solutions containing 0.009-0.45 M $FeCl_3$ and 0.001-0.3 M HCl.

The parameters that can be varied and are expected to show influence on the results are concentration of HCl and $FeCl_3$, time and temperature of reaction and increase of temperature as a function of time.

3.1 Description of the experimental procedure

Preparation

All glassware used is washed with demi water and millipore water and oven dried before use. Teflon bottles are cleaned by filling bottle and screw cap with concentrated sulfuric acid to dissolve eventual crystal remains. The bottles are left overnight, and afterwards they are washed thoroughly with demi water and millipore water and oven-dried.

Solid analytical grade $FeCl_3.6H_2O$ is dissolved by adding millipore water to obtain a 3.0 M stock solution. A stock solution of HCl is made using a plastic ampulla which on dilution to 1 litre gives a 1.0 M HCl solution. Millipore water is used for dilution. Stock solutions are kept in glass bottles. For experiment 7.1, the $FeCl_3$ is dissolved in the teflon bottle at once, while the HCl originated from a glass volumetric flask. On from experiment 21, all solutions are made and kept in polypropylene bottles to exclude the solutions from glass, which is probably the cause of the silicon found in the crystals.

Experimenting

Predetermined amounts of $FeCl_3$ stock solution and HCl stock solution are inserted into a 100 ml glass bottle with a pipette, and millipore water is added up to 100 ml. The solution is then filtered through an 0.22 μm millipore filter. Glass-free solutions are inserted into a plastic measuring cylinder with plastic pipettes, diluted and poured into the teflon containers. The silicon-free solutions are not filtered because the filter set is all glass.

30 ml teflon bottles are filled to ca. 3/4 with the solutions thus obtained, and some of the surplus solution is kept for analysis.

The screw-cap teflon bottles are closed and placed in an oven thermostated at 100 (+5) °C or at 65 (+4) °C. The bottles are placed two by two in a glass cup for eventual breakage and kept in the oven for 24 hours. After removal from the oven, the bottles are left to cool down to room temperature. They are then centrifuged in glass tubes for 20 min. at 2800 rpm. The mother liquors are decantated and stored in glass bottles for analysis, and the crystal mass is resuspended in millipore water acidified to pH circa 1.7 ($\pm$0.2) with HCl to prevent $Fe(OH)_3$ formation. The suspensions are again centrifuged and resuspended in acidified millipore water and stored in glass bottles. Some samples are kept in their mother liquors to determine the influence of washing with acidified millipore water, and some samples are stored in polypropylene to see if storage in glass affects the silicon content. Experiment 21.1 is partly stored in mother liquor and partly in glass after washing. The two parts are distinguished in this report by letter 'm' and 'g'.

Additional experiments

Some experiments are carried out to study the infuence of silicon. Of experiment 30.4, two drops (ca. 1 ml) of a diluted (ca. 0.001 M) $SiCl_4$-solution are added to half of the suspension after 3.5 hours. Of each half, half is put back into the oven. Experiment 30.1 is treated in the same way after 20 hours.

Production 17.1 is partly etched to see if silicon can be removed from the crystals. Etching is done by adding 3 drops of a concentrated NaOH solution to 6 milliliter crystal solution. Then millipore water is added until pH is circa 12. The suspension is left in the polypropylene beaker for 24 hours. Then the supernatant is removed with a pipette and neutral millipore water is added. After resettlement, the supernatant is removed again. The etched crystals are stored after the addition of millipore water.

A completely different way to hydrolyse the Fe^{3+} was carried out by slowly adding water to a solution of Fe^{3+}. The solutions originated from polypropylene bottles and poured into a polypropylene beaker. In one experiment, the solution was gently stirred; in another experiment the solution was left to stand. Water was added slowly, 10 to 20 ml of water per 10 minutes. After reaction had taken place, the solutions were treated as usual.

All experimental settings are listed in table 6. The experiments are described in more detail in the appendix.

3.2 Analyses

pH and Fe^{3+}-concentration

Of starting solutions and mother liquors, pH and concentration of Fe^{3+} were determined. Fe^{3+} concentration was determined with a spectrophotometer, or with atomic absorption spectrophotometry (AAS). pH was measured with a Corning-Eel digital 110 expanded scale pH-meter, using a combined glass electrode. The electrode was always calibrated at pH 2.00 and pH 4.00; solutions were analysed at room temperature. Until experiment 4, pH measurement was troublesome. The electode was very slow in response; it was too old. On from experiment 5, a new electrode was used, which gave more accurate results in much less time. Accuracy of the first measurements is estimated at ca. 0.05 in terms of pH, on from experiment 5, the accuracy is estimated at ca. 0.02. If the difference between two measurements exceeded 0.02, it was measured three times. One of the former values always was consistent with the new value. The accuracy of the spectrophotometric and the AAS determinations of $Fe^{3+}$are estimated to be 1 % each.

Transmission electron microscopy

Of the crystal solution, transmission electron microscope (TEM) samples were made on carbon-coated copper grids. At first a drop of solution was poured onto a grid at once with a syringe. Wetting of the grid surface was very poor, so later on millipore filtered acetone was added to the syringe content. The syringe was turned several times to promote mixing, and then a drop was put on the copper grid. Spreading of the crystals was much better then. A ratio of 3:1 acetone:crystal solution worked best, but results depend on the original crystal concentration. The method of preparation of the samples is listed in table 7.

TEM samples were inspected on either a Philips EM 400 electron microscope, with facilities for electron diffraction and elemental analysis, at the Laboratory of Materials Science, or with a Philips EM 201 electron microscope at the Laboratory of Microbiology.

X-ray analysis

X-ray exposures were made and analysed at the Laboratory of Materials Science. Samples were centrifuged, resuspended and again centrifuged, then resuspended in a little millipore water and dried in a 100 °C atmospheric oven or a 80 °C vacuum oven. Spectra were taken with a Guinier camera or, in case of smaller particles, with a turned Debye-Scherrer recording from millipore filter.

Sedimentation field flow fractionation

Until experiment 12, sedimentation field flow fractionation (SF_3) analyses were made, but the analyses did not offer reliable information due to the elongated shape of the particles.

Image analysis

Of the best production, image analysis was used to determine monodispersity. TEM-negatives were laid on a Wild M420 macroscope and imaged by a Joyce-Loebl magiscan 2a Image Analyser. Of the negatives, length, breath and area were determined, the results were analysed statistically.

Chapter 4: Results

The results of the experiments are presented in several parts. Observations made during the experiments are separated from the analyses made later. The analyses are presented method by method. The information obtained from experiments and analyses will be integrated in chapter 5.

4.1 Observations

Oven experiments

The presence of crystals was easy to detect. When crystals had developed, the solution became turbid. The colour of the suspensions in which akaganeite had formed was yellowish-brown, the colour of rust in water.

Not all experiments yielded β-FeOOH crystals. Several experiments did not yield any crystals at all. Experiments 6 and 18 resulted only in formation of hematite (α-Fe_2O_3). The colour of these suspensions was Indian red. The crystals settled much slower, and separation was incomplete after centrifuging 20 minutes at 2800 rpm. In experiments 11.2, 13.7 and 28, akaganeite was not the only crystal. At those experiments, a brownish yellow deposit, surrounded by a red ring appeared in the centrifuge tubes.

The experimental results are presented in table 8 in descending order of pH, with their crystal form. If no remarks are made, akaganeite was the only crystal present. As production of β-FeOOH is of main interest, the other experiments will often be regarded seperately in the following analyses.

Centrifuged crystals usually redissolved readily, but sometimes a thick brown cake was left that redissolved only with great difficulty. This coagulated matter was darker than the crystals that redissolved readily. The colour difference was probably caused by a difference in reflection, because when the crystals did eventually dissolve the colour was normal again.

Addition of water to centrifuged crystal mass gave a whitish-yellow suspension, containing $Fe(OH)_3$. Suspensions containing $Fe(OH)_3$ stayed turbid even after centrifugation, because the $Fe(OH)_3$-particles were very small. To prevent formation of $Fe(OH)_3$, crystals were washed and stored in acidified water. Only when crystals had to be dried, neutral water was used after repeated washing.

The $FeCl_3$ stock solution was stable; it did not develop crystals in half a year. Starting solution 17.1, however, developed crystals, most probably akaganeite, during prolonged storage at room temperature.

One of the experiments, number 24, did not produce crystals at 65 °C after 24 hours. One of the two samples then was placed in a 100 °C oven. Crystals did grow then.

During heating of the starting solution, the colour of the solutions changed from pale yellow to darker yellow, or from darker yellow to brownish yellow. This can be an indication either for increased hydrolysis or for the presence of Fe^{2+}, though Fe^{2+}-solutions mostly are coloured greenish. The absence of ferrous ions can be proved by measuring the redox potential of the solution. This was not done due to lack of time.

S-experiments

The S-experiments, in which ferric ion solutions were diluted slowly, were carried out for two reasons. One was to see if heating the solution was a similar process to normal hydrolysis processes, and would thus give similar results. The other reason was to see if a different way of effecting hydrolysis would give bigger or more uniform crystals.

The experiments at which water was slowly added to the ferric solution differed greatly due to stirring. In the unstirred experiment, solution and water did not mix well. A two-layered structure appeared and remained. The first day the solution was clear. After 3 days, the bottom was covered with whitish coagulated matter. The colour of the solution had turned darker. The fourth day, the solution still had whitish coagulation, but beneath it, a rust-coloured layer arose. This layer grew somewhat in the following days. After 7 days, the crystals were separated by centrifugation as usual.

The stirred experiment was gently stirred from the time the water was dripped into the solution. The solution mixed well, and there was no colour difference. The solution was left for 8 days while being stirred, but nothing happened. The colour had turned a little darker yellow, though. Stirring was stopped and still nothing happened for about two weeks. After the solution had stood for another month, crystals had developed.

4.2 Analyses

The results of the various analyses that have been performed to characterize the crystals and to determine the experimental conditions are shown below. In order of appearance, pH and ferric ion concentration, evaporation losses, yield, image analysis, x-ray diffraction, transmission electron microscopy, sedimentation field flow fractionation and some remaining analyses will be presented.

4.2.1 pH and Fe^{3+}-concentration

pH and Fe^{3+}-concentration were determined to characterize the solution from which the crystals had grown. All pH- and Fe-measurements are listed in table 9. Fe-content and pH of all productions were determined before and after crystallization. Measurement of the Fe^{3+} concentration was done spectrophotometrically until experiment 13. From 14 on, analyses were mainly Atomic Absorbtion Spectrophotometry (AAS)-measurements.

The first AAS analysis-results were distrusted for three reasons:

- Of one solution, analysed by the two methods, the measured concentrations showed 20 % difference.
- Input Fe^{3+}-amounts were not expected to be systematically too low.
- Of many starting solutions, Cl^--concentration was determined. Its aim was to verify HCl concentrations. However, chloride from $FeCl_3$ had to be subtracted from the total amount of chloride present. In case of spectrophotometric Fe^{3+} determination, a reasonable number of HCl concentrations was in agreement with the HCl input, i.e. within ca. 5%. With AAS determination of Fe^{3+}, however, almost all HCl-concentrations were orders of magnitude too high. When the expected Fe^{3+} concentrations were used, HCl-concentrations were in agreement as well.

After several checks, discrepancy between measured and expected values could be attributed to formation of $Fe(OH)_3$ in the diluted samples, as they were to be measured. Formation of $Fe(OH)_3$ did not disturb the measurements when one or a few experiments were done, because samples were shaken before analysis. An automatic sampler was used for large amounts of samples, which resulted in sedimentation of $Fe(OH)_3$. This led to underestimation of the ferric ion concentration. The samples were analysed by hand. Results agreed better then, though results from different methods are still not fully matching. The Fe- and Cl-analyses are presented in table 10.

The difference between the various ways to obtain the Fe^{3+}-concentration gives an idea of the origin and kind of errors that are made. When difference between the three different Fe^{3+}-concentrations was small, no large errors were made. When one of the concentrations is different from the other two, that concentration may be erroneous. For instance, when expected input and calculation via Cl^- are similar but measurement is different, the Fe^{3+}-measurement may be distrusted. This comparison of the various estimations reveals the following possible errors:

- Over 10 % input errors in 11.2 and 12, 5 to 10 % input errors in experiments 6.2, 26, S2.
- HCl input errors in experiments 5.2 and 10.
- Fe^{3+}-measurement errors in experiments 6.1, 9, 13, 14, 15, 16, 18 and 24.
- Of experiments 7.1 and 18, input errors could be traced back to calculation mistakes, so their input values were adjusted.

Of course, these errors are only an indication of what went wrong. When for instance two methods are similarly bad, the third value is distrusted wrongly.

4.2.2 Evaporation

Evaporation losses during the experiments were determined at several experiments by weighing, to see whether the final ferric ion concentration was influenced by the evaporation of water. At experiment 1 weights were determined. This first experiment was performed with teflon beakers with a lid instead of a screw cap, so considerable evaporation was expected. Evaporation losses were 11.4 % at experiment 1.1 and 31.5 % at experiment 1.2.

Of the 7 productions of experiment 13 (100 °C), all weights were determined. Of 21 grams starting solution, weight loss was 0.09 grams on an average, with a peak value of 0.24 grams, so 0.4 % average weight loss, up to 1.1 % maximum. Conclusion from experiment 13 is that evaporation was negligible at experiments not exceeding 100 °C.

Experiments at temperatures above 100 °C are expected to show more evaporation, which is confirmed by the increase of ferric ion concentration during the experiment.

4.2.3 Yield

From disappearance of $Fe^{3}+$ and an average production volume of 25 milliliter, an estimation can be made of the experimental yield (see table 11). Some of the estimations were negative. This is mostly due to evaporation of water in experiments that did not yield crystals or to temperatures above 100 °C. The only negative productions left then are 23 and 20.2. Estimated yields are presented in table 11, in which negative values are set at zero. Two productions have been dried entirely to check the estimations. Experiment 13.4 had a theoretical maximum yield of 0.10 grams. After drying in an oven at circa 80 °C 0.06 grams remained. Not bad, in view of firstly losses due to repeated decantation, and secondly a possible 10 % loss of weight according to Mackay [mac60] at heating to 100 °C. Experiment 27.2 was expected to give 0.06 grams of material, and after drying 0.05 grams were left. It may be concluded that estimations of yield are quite reasonable; the order of magnitude is certainly right. The number of crystals that is obtained by the best experiments (estimated yield 0.01 to 0.02 grams) is in the order of 10^{11} crystals, as one crystal has a volume of circa $1.5 \cdot 10^{-19}$ m^3, and 1.5 grams of crystals has an estimated volume of $1.0 \cdot 10^{-8}$ m^3.

4.2.4 Image analysis

Of the best production 21.1 (g & m) monodispersity was determined more fundamentally than by rough estimation only. Length, breath and area were determined from the transmission electron microscope negatives by image analysis with a macroscope. Results are to be distrusted a little for two reasons. One is that illumination could not be adjusted such that the end of one fibre laying on another could reveal the real end. Instead, a situation as shown in figure 12 appeared on the screen. The other reason was that overlapping fibres that were not subject to the previous problem and twins would largely disturb measurements. For that sake, those fibres were adjusted by erasing the opposite ends of one respectively two of the X- or star-shape constituent fibres (see figure 12), or by erasing the left-over part of the fibre overlapping with the measured one. The first factor causes a systematic underestimation of the fibre length, the second factor has an unknown effect on the results.

The results of the image analysis are shown in table 13. On the basis of those results, the samples can be called monodisperse. However, in reality they are not due to the presence of stars and parts broken from the stars, which I named "broken legs".

Experiment 21.1 m was analysed seperately to exclude possible differences due to washing. The elumination problem mentioned above may have had a worsening influence on determining length and aspect ratio. The fibres that were not lying on others were systematically longer and had a larger aspect ratio than the ones that did not coincide.

4.2.5 X-ray diffraction

To reveal the crystalline structure of the synthesized materials, X-ray analyses were done with several productions. Crystals from experiments 1.1 & 1.2, 6.2.a and 7.1 were analysed by X-ray powder diffraction. All crystalline material of experiment 1.1 & 1.2 was indentified as β-FeOOH. Taking the accuracy into account, it means that 95% or more of the crystalline material was β-FeOOH.

The crystals from experiment 6.2.a were indentified as hematite, α-Fe_2O_3, which was already expected due to the Indian red colour.

Experiment 7.1 was analysed because on TEM pictures small spherical particles were present besides the fibres. X-ray analysis, however, indicated a β-FeOOH pattern in which no contamination could be seen. This means that contamination was either under 5 %, or had a crystal structure similar to β-FeOOH, or it was β-FeOOH.

4.2.6 Transmission electron microscopy

On the transmission electron microscope the fibres were analysed in different ways. The fibres were viewed and photos of them were taken to measure the crystals and to compare them with other crystal productions. Electron diffraction photographs of the crystal structure were made to identify the crystals. Finally the fibres were subjected to energy dispersive spectroscopy (EDS), by which an elemental analysis of the fibres is obtained. The results of the three analyses are presented below.

Transmission electron microscope images

On some of the electron microscope photos a transparent layer is seen on the outside of the crystals (figure 14). The layer is more distinct on photos from the EM 201-microscope. The difference may be caused by the advanced techniques to improve the contrast present at the EM 400 electron microscope. A diaphragm is used with this microscope that makes the crystals much darker. This technique may result in poorer visibility of the transparent layer. Maybe the diaphragm also influences visibility of amorphous structures. Little effect is to be seen on the EM-400 photos as well (see photo 7.1 number 31). A transparent layer is slightly visible at the top.

A phenomenon seen at experiments 30.1.1, 30.1.2, 30.2, and a little at experiments 20.1, 21.1 and 23.1 is the presence of two size classes of crystals (see 30.2 photo 65, figure 16). This may be caused by secondary nucleation.

The non-etched 17.1 sample fell apart by electron damage. The surface of the etched crystals looks more porous when compared to normal surfaces. Comparison with non-etched 17.1 surface is not possible because of the electron damage.

Production 21.1 was analysed on TEM twice. Part of the production was poured from the teflon bottle with a syringe at once onto copper grid; part was treated as usual and stored in glass before it was put on the grid. TEM photographs did not show difference in length or form of the crystals, but the crystals in mother liquor seem to have a rougher surface.

Washing is to be preferred when electron microscope images are made, because contamination of the samples with dirt is much less. Unwashed samples, like samples 30.4.1, 30.4.3 and 7.1 give poor quality samples, though other samples sometimes are dirty as well. Washing also removes dirt from the crystals, making them better suited for their later use.

Based on the electron microscope images, several parameters were given to the various crystal productions. Crystal length and breath were measured, aspect ratio was calculated. Sizes determined using the electron microscope images may have an inaccuracy of 5 %, due to imperfect adjustment of the lenses. Uniformity was determined by rough estimation; productions were given marks 1 to 5 in ascending order of uniformity. Apart from that, the shape of the crystals was described in terms of block, needle, cigar- or spherical shape. The presence of twins is indicated by a letter 't'. These quantities are shown in table 15. Examples of the TEM-images are presented in figure 16.

Electron diffraction

Electron diffraction patterns of several crystals were made with the EM 400 microscope. Diffraction pattern photos were made of the experiments 1.1 & 1.2, experiment 4.1, spherical crystal of experiment 7.1, a fibre and a star of experiment 21.1. Experiment 1.1 & 1.2 and both shapes of experiment 21.1 could be indentified as β-FeOOH. Experiment 4.1 and 7.1 gave no unambiguous results when compared to several iron (hyrd)oxide d-values.

Manual comparison of the spectra is tedious and does not easily lead to the right crystal. As the manual comparison did not offer results, d-values were matched against a JCPDS-database at the AKZO Research Laboratory in Arnhem. All d-values were given intensity 100 and compared to a large set of iron oxide crystals. Best fit for both compounds was FeOOH, an orthorhombic crystal formed by heating β-FeOOH. However, a disadvantage of the electron diffraction patterns is that they do not match intensities of the X-ray pattern tables (JCPDS-cards). Control by naming all the spots did not affirm the result obtained with the library search. Conclusion is that patterns may be some patterns of β-FeOOH which were affected in some way by the electron beam, as the patterns do match the β-FeOOH pattern to a moderate extent.

Elemental analysis

The first elemental analysis was carried out to see if the crystals contained chloride. The analysis pointed out that chloride was indeed present, but also that silicon was present. This was not expected. For this reason elemental analyses by energy dispersive spectroscopy (EDS) were performed routinely. The detection limit of EDS is the element sodium (Na); elements whose atomic number is less that that of Na can not be detected. The presence of the detected elements (apart from iron) is discussed seperately below. All elemental analysis results are presented in table 17.

The detected amount of chloride varies between 0.8 and 18.8 atom % - rather a large variation. The amount of chloride present does not seem to have any relation with any other aspect of the experiments. The influence of washing, which is known to effect the chloride content, cannot be traced here. As stated by Mackay [mac60], chloride content of β-FeOOH is initially about 1/4.79 * Fe content, while it drops on repeated washing. This effect did not occur with the present experiments. At these experiments the chloride percentage is sometimes higher and sometimes lower than 1/5 of the iron percentage. Besides, the iron percentage of samples made directly from mother liquor does not differ significantly from the washed samples. The chloride content of experiments 1.1 & 1.2, 7.1, 21.1 m, 30.1.1, 30.1.3, 30.4.1 and 30.4.3 should have been higher than others if washing lowers the chloride content. However, the opposite occurred; experiment 21.1 m contains less chloride than 21.1 g, while experiments 1.1 & 1.2 and 7.1 tend to less chloride than average. Experiments 30.1.1. and 30.1.3 finally have a perfectly normal chloride content.

The presence of silicon was not expected at all. Silicon was present in almost all crystals produced. Thorough examination did not reveal its origin.

The silicon content of experiment 7.1, made from solid $FeCl_3$ dissolved in teflon equipment, was less than usual, but not as low as was expected when glass would be the origin of the silicon. Experiment 21.1 m, at which all reactants came from polypropylene equipment instead of from glass, showed silicon was still present. As experiment 21.1 m had a higher silicon content than 21.1 g, storage in glass proved not to increase the silicon content.

Of production 17.1, part has been etched to see if the silica layer could be removed. The not-etched crystals immediately fell apart due to electron damage, whereas the etched crystals did not. Silicon content had not altered due to the etching, chloride content was lower at the damaged sample; it had an atom % of 2.6 versus 5.3 for the etched sample.

The presence of sulfur is slowly increasing during the experiments. Its presence is most striking at experiment 30, where sulfur is present in several atom %.

On some samples the extraneous elements arsenic (As) and potassium (K) were also detected. In production 12.1 as much as 19 % As was found on one place, and chromium (Cr) and titanium (Ti) were also found. Production 7.1 also contained some arsenic. The presence of these elements can only be explained by an accident that happened while preparing the samples. One of the samples, most probably 12.1, fell on the laboratory table at the electron microscope while it was drying. The sample and the pincet must have become contaminated with those elements. The pincet could have spread the contamination at another grid that wetted the pincet again. This could have been sample 7.1.

Small area EDS has been used to study the distribution of silicon in a crystal. Of three crystal productions, one crystal each has been analysed. Measured spots are shown in figure 18; the analysis results are shown in table 19. It must be noticed that measured values are an indication of the presence of silicon, but they must certainly not be considered absolute for two reasons. An extremely small electron bundle always causes growth at the spot. The suppleted material disturbs the detection. Because of this growth, measurements are stopped earlier, when the ratio of signal to noise is in fact too small.

4.2.7 Sedimentation field flow fractionation

Sedimentation field flow fractionation (SF_3) was tried because a fast and reliable analysis of the size of the produced crystals was wanted. Until experiment 12, SF_3 analyses were made of the crystal mass. The cumulative number d_{50} and d_{50}/d_{16} and d_{84}/d_{50} are listed in table 20 and compared with the TEM results. Size and monodispersity measurements both were incoherent. No more SF_3 analyses were carried out, because the accuracy seems poor when analysing fibres.

4.2.8 Other analyses

The silicon content of the glass-free starting solutions was measured to see if reactants could be the origin of the silicon. AAS-determination of silicon-amounts in the millipore water, the 1 M HCl in millipore and the $FeCl_3$-solution in millipore proved this hypothesis to be false. Contents were 14 ppb, < 10 ppb and 130 ppb respectively. These concentrations could not lead to more than $1.5 * 10^{-3}$ milligram Si present in a production of 0.05 M Fe. For an amount of Si of 5 % in an average production, as much as 2.88 milligram Si is necessary to cover all crystals. This means silicon did not originate from the pro analysis reactants.

Fibres were dissolved in 96 % H_2SO_4 to analyse the Si-percentage of the fibres. Crystal mass and/or silicon did not dissolve completely, a whitish flocculent solution was obtained. The AAS analysis did not show a significant concentration of silicon, less than 0.5 ppm Si was detected. However, this result was to be expected, as not all silicates dissolve in sulfuric acid. The flocculent must have contained the silicon.

Magnetic properties of the crystals were tested by holding a magnet to the sample bottles. Neither hematite nor akaganeite reacted to the presence of the magnet. Holding a needle in the crystal suspension did not cause any movement in the crystal mass either.

In the next chapter conclusions will be drawn from all the above analyses of the experiments and the theory that lays behind the experiments.

Chapter 5: Discussion

In this chapter, many aspects of the growth of akaganeite are discussed. The chapter deals with the following characteristics of the produced fibres: limits to the growth region of akaganeite, shape, size and monodispersity of the crystals, reproducibility of the experiments, the presence of silicon and of twins, and the advancements made during the course of the work.

5.1 Advancement

The following results have been obtained in half a year:

The influence of different parameters on the growth of akaganeite has been determined. Related problems in the growth of crystals, like the presence of silicon and the presence of twins, have been studied and some of them have been explained theoretically.

A theory accounting for the non-uniform growth shape of akaganeite was found in the literature.

The reaction mechanism was sought in the literature as well. It is presented as far as it is known.

Compared to Matijevic's results, the length of the fibres is increased from 0.25 μ to over 1 μ, which is much more in the direction of the desired fibre length (2 μ). This has been achieved without loss of monodispersity.

5.2 Growth

Growth of akaganeite is only possible within certain conditions. The most important condition is the acidity of the solution. The ferric ion concentration plays a minor role. Too low a pH does not cause enough hydrolysis, and crystals will not grow. Too high a pH causes too much (or too fast) hydrolysis and causes the colloid to loose more H_2O. An iron oxide like Fe_2O_3 will then result. Between about pH 1.00 and 2.00 akaganeite can be made (see table 8); at the lower extreme, a high ratio $FeCl_3/HCl$ (10/1 instead of 1/1) does give yield longer. The higher the starting pH is, the more hydrolysis takes place, as is shown by the larger decrease in pH (see table 8).

The limits to the growth region of akaganeite are not completely similar to the limits Matijevic found. Some of my experiments (2.1, 2.2 and 15) in which no crystals grew, belong to a region where Matijevic reports the growth of rods. Two other experiments that did not yield crystals were not in disagreement, one was outside the range he measured in, and one had no yield at his experiments as well. I do not know the reason for these contradictory results.

The conditions at which he obtained hematite instead of akaganeite are similar to mine.

Crystal growth is influenced by reaction time and reaction temperature. The higher the reaction time, the lower the reaction temperature necessary and vice versa. The role of temperature is shown clearly in experiment 24, where crystals did develop at 100 °C, but not at 65 °C. The role of time is shown in experiment 30.4, where three hours were not enough to develop crystals, while after a day, crystals had grown.

The reaction is known not to have reached completion after a day. Matijevic performed experiments lasting a week. Many of the solutions that yielded akaganeite after a day had turned into hematite after a week. Experiment 13 shows this effect as well; the experiment that lasted in the oven for three days already contained some hematite.

5.3 Shape

Akaganeite fibres have been made in several shapes. Oblong and non-uniform fibres can be made with relatively high Fe concentration and correspondingly low pH. At higher pH's and lower ferric ion concentration, thick-set and more uniform crystals grow. Cigar shapes develop at 65 °C under conditions that give block formation at 100 °C.

In his publication Matijevic mentioned the presence of needles only, while I have grown cigar-shapes also. The cigar-shapes which I grew developed at 65 °C, a temperature at which he did no experiments.

The statement of Matijevic that higher pH results in shorter and more regular fibres is corroborated by the present experiments.

Aspect ratio is clearly connected with pH: the lower the pH of the sol;utions from which the crystals grow, the higher the aspect ratio. Between ferric ion concentration and aspect ratio, no relation can be shown. Relations between aspect ratio and pH, and between aspect ratio and Fe^{3+}-concentration are shown in figure 21.

5.4 Size

The average length of the fibres varied between 0.2 μ and 2.0 μ. The maximum length that can be obtained might increase when the presence of silicon can be excluded to a greater extent than in the present experiments.

Increasing the length of the fibres may also be achieved by using crystal growth techniques. Three possibilities that should result in larger crystals are:

- addition of base to maintain a higher pH in order to continue hydrolysis;
- installing a temperature programme on the oven so as to obtain a lower supersaturation rate;
- seeding with very small seeds at a low supersaturation rate.

All those methods increase the growth time at the cost of nucleation.

In the theory two factors are presented that can cause a low supersaturation: a low pH and a low concentration of Fe^{3+}-ions. As longer fibres occur at lower pH, pH appears to influence the size. Two other observations support this idea: Comparison of experiment 17, 19 and 22 reveals an increase in crystal size when amount of HCl is increased at constant Fe^{3+}-concentration. Comparison of experiment 30.2 with 30.3 also shows that crystals are larger when more HCl is added.

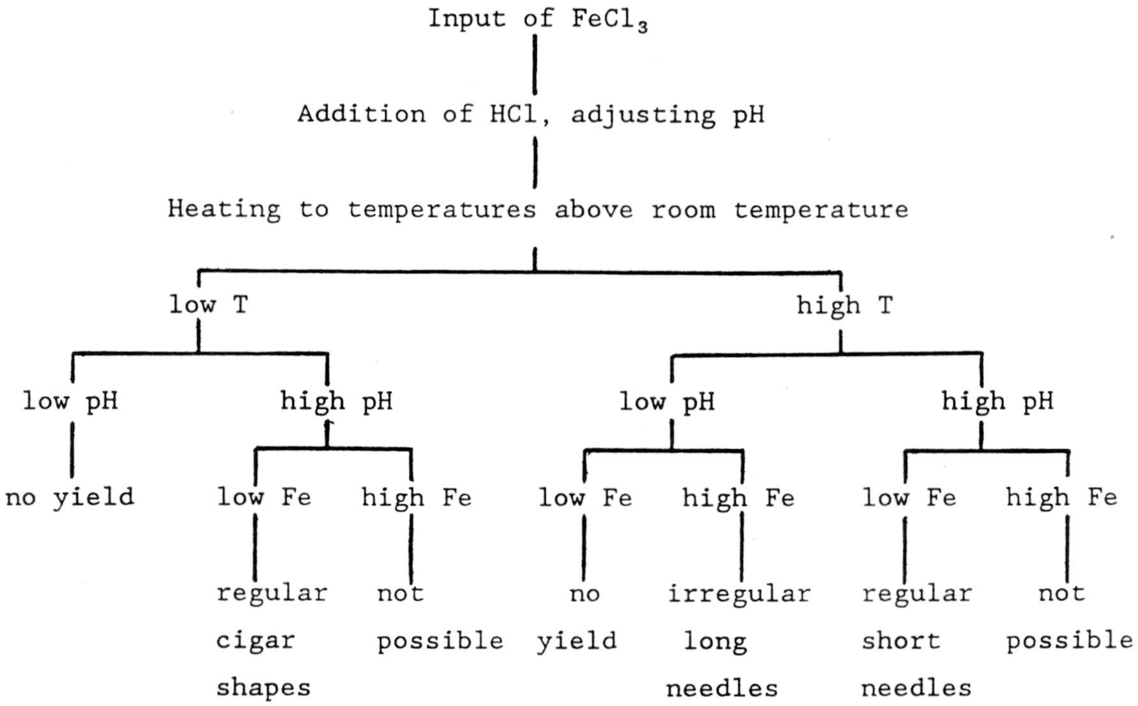
The influence of pH and ferric ion concentration on length is shown in figure 22. Figure 22 shows no relation between ferric ion concentration and length. For a good comparison experiments with different ferric ion concentration having a similar pH should be compared. The most suitable experiments for comparison are experiments 12.1 and 11.1.a. The crystals of experiment 11.1.a, containing more iron, appear to be larger. This is not in accordance with the supersaturation theory. Accoring to this theory, lower ferric ion concentration leads to larger crystals. No explanation for this difference was found.

5.5 Monodispersity

The influence of pH and ferric ion concentration on monodispersity are shown in figure 23. The monodispersity increases with increasing pH and decreasing Fe-concentration.

Theoretically monodispersity of crystals can be promoted by a long growth time in which no nucleation can take place, thus: a long period of low supersaturation. Theoretically, low pH and low ferric ion concentration should lead to monodisperse crystals.

Experiments with similar Fe^{3+}-concentration and different pH show a decrease in monodispersity when HCl-concentration increases. This is opposite to what the theory predicts. The influence of the ferric ion concentration is in accordance with theory: low concentration of Fe^{3+} does lead to increase in monodispersity. After determination of the above parameters growth size, shape and monodispersity, the following scheme can be presented:



5.6 Reproducibility

Many of the experiments are carried out in duplicate. The results of these duplicates in terms of pH and ferric ion concentration at the end of the experiment are similar, but they are never identical. Crystal growth is either very sensitive to extremely small differences, or a factor that is not studied is influencing the growth (e.g. small differences in production volume). The duplicate experiments are never both analysed on TEM. However, some experiments having similar conditions can be compared by quantities obtained from TEM images. Comparison of these experiments (4.1 and 16, 11.2 and 17, 21.1 and 22.1) shows satisfying similarity in length and aspect ratio. Slightly different pH or ferric ion concentration leads to a substantial difference in solution characteristics at the end of the growth, but the size and shape of the crystals appears less sensitive to small changes.

5.7 Silicon presence

The mechanism by which silicon disturbs the growth of akaganeite was not discovered. Experiment 30.4 was meant to explainte part of the mechanism, but the experiment was unsuccesful. The TEM-samples of experiment 30.4.1 and 30.4.3 were of a bad quality (one has been photographed, see figure 16) and experiment 30.4.2 and 30.4.4 had not developed crystals. When it appeared the removed bottles had not grown crystals, experiment 30.1 was treated the same way the next morning. Experiment 30.1 had developed crystals then, but crystal growth did not proceed much more after the addition of silicon. As the difference between the four solutions is very small, results of experiment 30.1 are not very reliable. The conclusion that can be drawn from experiment 30.4 is that crystals can develop when high concentrations of silicon are present. Of experiment 30.1, only the crystals that were heated again after addition of silicon did contain a higher concentration of silicon. This shows silicon is included in the crystals at higher temperatures only.

The origin of the silicon has not been traced. The high amount of silicon in the S-production, which was left in open air for several days, makes me believe that silicon is present in the laboratory air. This becomes more plausible as in former experiments silicon carbide was used in the fume cupboard in which I performed my experiemnts.

After the conclusion on the possible presense of silicon in the air, the idea arose that the high amount of sulfur present at experiment 30 may have been caused by dust in the air as well. Between experiment 29 and 30, the fume cupboard had been used for dust explosions with maize flour. Being organic material, the only element above the detection limit of EDS it contains in reasonable concentrations will be sulfur. Maize flour may even contain more sulfur, as a sulfur compound is used at the production of maize flour. This coincidence does support the idea of contaminating dust in the fume-cupboard air. It must be mentioned that this idea arose because of the former suspicion on dust. Logical reasoning prohibits supporting a theory by an idea that has been derived from this theory, so this statement is not a support for the theory that dust in the air is a cause of contamination.

The hypothesis of Kuhnel that silicon would concentrate on the outside of the crystals was affirmed by elemental analysis of small areas of a crystal. The walls contain much more silicon than the centre. The small concentration of silicon detected at the centre may even be due to the surface that encloses bottom and top of the detected cylinder.

5.8 Twinning

Twins are found only in the productions with blocks (low aspect ratio needles) and cigars. It is, however, possible that twins would exist at needle-shaped productions as well, if they would not break down soon after their development. To study prevention of twin formation, use is made only of the cigar- and blockshaped productions.

When cigar- and block shaped productions are screened on their relative amount of twins (see table 24), some experiments do have non-standard twin values. Experiment 17.1 has a lower twin percentage than usual, while several productions are above normal. Experiment 17.1 and 25.1 differ only in amount of silicon and in concentration of HCl. The presence of more HCl at experiment 25.1 thus accounts for the presence of far more twins. Conclusion may be that higher concentrations of HCl promotes twin formation. Unfortunately, low HCl concentrations, preferable in view of twin formation, decreases the length of the fibres. Aspect ratio seems to have direct influence on monodispersity. The lower the aspect ratio was, the better the monodispersity. The theory that twins occur due to a lack of hydrolysing water is supported by experiment. Low HCl concentration releases more hydrolysing water, and less twins are indeed formed. Apart from that, the theory is supported by the configuration of the twin plane. If shared OH-groups are the reason for twinning, the shared plane must consist of lots of OH-groups. When the unit cell content is considered, the (332)-plane crosses the atomic planes as shown in figure 25. Indeed it crosses only OH-groups. Building a scale model of the unit cell may give more insight into this matter.

Chapter 6: Conclusions and suggestions

For funcionality, conclusions and suggestions have been separated from each other. The conclusions are presented first.

6.1 Conclusions

Not all experimental findings led to conclusions. Many of the experimental findings could not be explained theoretically. The number of experiments that was performed and the incompleteness of theory do not allow clear predictions concerning what might happen at experiment that differ from the present ones. In other words, there are far too few data to be able to do reliable predictions. The following tentative conclusions are presented:

- The monodispersity of the produced fibres is very promising. When stars can be removed, monodispersity will be within the 10% range. Centrifuging removes a lot of smaller dirt.

- The role of silicon in the growth process of β-FeOOH is not fully understood. Exclusion of silicon was not obtained. When this is effected, more insight in its influence on growth of akaganeite may be obtained. The exclusion of silicon is expected to lead to larger fibres.

- Twinning is promoted by addition of more HCl. As this conclusion is based only on one experiment, this conclusion is probably not very reliable. More experiments will be necessary, if this phenomenon is to be better understood.

- The theory of shared water molecules causing the growth of twins is supported by the above conclusion that more HCl leads to more twins, and by the content of the (332) plane in the unit cell.

- Lower crystallization temperatures are preferable, as the most uniform fibres were produced at that temperature. Slower hydrolysis, as with experiment S 1 and 2, seems preferable, but a wider size distribution is found. Furthermore, the oven process is faster and easier to control and to reproduce.

- Reproducibility of the experiments is only moderate. When an amount of identical crystals is wanted, it must be made in the same batch.

- The crystals are rather short, 1.2 μ, but the crystals are big enough to disperse them in a lung model.

- Aspect ratio of the crystals, ca. 5, is sufficient to call the crystals fibres, but variation of the aspect ratio while maintaining uniformity could not be realised.

- Theory on the formation of akaganeite appears to be incomplete. Especially the steps following the hydrolysis are unknown. Recent literature may reveal some of the theory lacking.

- The growth shape of akaganeite is explained by crystal growth theory. The theory shows other fibre-shaped crystals can be expected at crystals that have one plane with low indices with short interplane distance, perpendicular to planes with long interplane distance.

- The conditions at which the longest uniform fibres were made are: temperature circa 65 °C, oven residence time 24 hours, concentration of $FeCl_3$ around 0.05 M and of HCl circa 0.01 M, pH_{start} is circa 1.77. Length of fibres produced in this way is circa 1.2 μ, aspect ratio circa 5.

6.2 Suggestions

Suggestions can be given at different levels, depending on the interest of the user. The suggestions are therefore separated in suggestions for theoretical support, for thorough practical investigation and for relatively simple improvements of presently used techniques.

- The process of growth of akaganeite still demandsng theoretical explanation. Occurence of twins, inclusion of silicon, and reaction mechanism are interesting subjects that are only partly understood. The function of supersaturation and the reason why sometimes hydrolysis capacity and sometimes ferric ion concentration are the dominant steps also needs theoretical investigation. The use of theoretical understanding on the growth of uniform crystals is only indirect.

- More attention to crystal growth techniques, as mentioned in the discussion chapter, may be promising. Investigations in that direction need close cooperation with the crystal growth section. The only disadvantage is the amount of time required. I think that for such work a student working parttime or fulltime at the industrial crystal growth section is necessary. A personal opinion that may be completely wrong is that when not performed on larger scale, industrial crystallization techniques are inapplicable or will decrease process control and reproducibility of the experiments.

- A simple experimental improvement that is less time-consuming than the preceding suggestions must be expected in the exclusion of silicon. Exclusion of silicon is expected to lead to larger crystals. The only improvement that is necessary for the present crystal productions is removal of twins. Centrifugation, probably sedimentation field flow fractionation, may prove a good technique. The fibres that can be obtained in this way will undoubtedly be usefull for fibre inhalation studies using a lung model.

Epiloog

De indruk die ik heb na een half jaar werk is dat er in die tijd geen nieuwe of unieke resultaten te boeken zijn. In een half jaar kun je niet van nul af aan een dusdanige expertise opbouwen dat je dingen kunt bereiken die anderen niet al beter konden.

Ik denk dat het beter zou zijn een student die zo'n onderzoek doet te sturen naar een plaats waar expertise op het gewenste gebied aanwezig is. In een dergelijke omgeving is sneller en meer resultaat te boeken, denk ik. Een half jaar onderzoek kan wel nuttig zijn om zelf wat van te leren, maar helpt het project of de wetenschap minder vooruit dan zou kunnen.

Ik denk ook dat de aandacht voor vooruithelpen van de theorie met behulp van experimenten en het boeken van materieel resultaat de hoeveelheid resultaat negatief beinvloedt. Een soort 'van-alles-wat'-opstelling kan nooit een diepgaand resultaat opleveren. Bij mijn onderzoek was het echter wel een soort van-alles-wat: het maken van vezels, begrijpen waarom de kristallen vezelvormig zijn, weten hoe de kristallen ontstaan, ingaan op fundamentele aspecten van de groei van tweelingen en de aanwezigheid van silicium. Als een onderzoek over zoveel aandachtspunten verdeeld is, kan het geen vergaande resultaten opleveren.

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