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THE EFFECTS OF VARIOUS PRECIPITATION CHEMICALS ON THE PROPERTIES OF ALUMINA-BASED HYDROXIDES

Degree Programme of Chemical Technology
2009

ABSTRACT

THE EFFECTS OF VARIOUS PRECIPITATION CHEMICALS ON THE PROPERTIES OF ALUMINA-BASED HYDROXIDES

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Degree Programme in Chemical Engineering
March 2009
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UDC: 66.01, 669.71
Number of pages: 76 (+13)

Key words: aluminium, amorphous compounds, crystals, precipitation

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Titanium dioxide pigment is surface treated with various inorganic hydroxides. The purpose of a coating is to optimise processability as well as the chemical and physical properties of the TiO_2 pigments. The treatments are tailored to the requirements of the final application. The most important surface treatment compound is aluminium hydroxide.

This work was based on a previous study of pure alumina precipitations carried out by Tuomo Keskisaari. In addition to aluminium, in this study silicon, phosphorus, zirconium and titanium hydroxides were precipitated. One of the main interests was in the effect of the selected surface chemicals on the crystallinity/amorphocity of the aluminium hydroxide. The sodium and sulphate contents of the precipitate were also of interest.

Three different precipitation series, with twelve different surface treatment combinations, were prepared. Two of the precipitation series were based on acidic aluminium sulphate, and the third series was based on basic sodium aluminate. The acidic precipitations were precipitated with mixed NaOH and Na_2CO_3 up to pH 6 and pH 8. The basic precipitations were precipitated with sulphuric acid down to pH 7. Precipitation temperature, precipitant addition rate and concentrations of the precipitations were constant. The filtration, washing and wet cake drying methods were selected according to the previous experimental study carried out by Tuomo Keskisaari.

In basic combination precipitations the presence of silicon created amorphous aluminium hydroxide with some crystalline elements. The other basic precipitated samples, which did not contain silicon, were crystalline bayerite or a combination of bayerite and boehmite. The acidic precipitated samples were pseudoboehmite phase, either pure amorphous or amorphous with some crystalline boehmite elements.

The crystallinity of the aluminium-based hydroxides had an effect on various chemical and physical properties of the precipitate. The pure amorphous samples were more porous than the amorphous samples which contained crystalline elements or crystalline samples. In acidic combination precipitations, the sodium and sulphate content was reduced in comparison to the pure alumina sample: the sodium content increased and sulphate contents varied in the basic precipitations.

TIIVISTELMÄ

ERILAISTEN SAOSTUSKEMIKAALIEN VAIKUTUS ALUMIINIHYDROKSIDIN OMINAISUUKSIIN

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UDK: 66.01, 669.71
Sivumäärä: 76 (+13)

Asiasanat: alumiini, amorfiset aineet, kiteet, saostus

Titaanidioksidipigmentti pinnoitetaan erilaisilla epäorgaanisilla hydroksideilla. Pinnoitteiden tarkoitus on parantaa TiO_2- pigmentin prosessoituvuutta sekä lopputuotteen fysikaalisia että kemiallisia ominaisuuksia. TiO_2- pigmentin pinnoittamiseen käytettävät epäorgaaniset hydroksidit valitaan pigmentin käyttötarkoituksen mukaan. Alumiinihydroksidi on tärkein pigmentin pinnoitteena käytetty hydroksidi.

Tämä opinnäytetyö on jatkoa Tuomo Keskisaaren aikaisemmin tekemään diplomityöhön, jossa tutkittiin saostamalla saatuja alumiinihydroksideja. Tässä työssä saostettiin alumiinihydroksidin lisäksi pii-, fosfori-, zirkonium- ja titaanihydroksideja. Tutkimuksen painopiste oli valittujen pinnoitekemikaalien vaikutus alumiinihydroksidin kiteisyyteen/amorfisuuteen, sekä natrium- ja sulfaattipitoisuuksiin saostetuissa lopputuotteissa.

Erilaisia saostuksia tehtiin kolme sarjaa, joissa kussakin oli 12 erilaista kemikaaliyhdistelmää. Kaksi sarjaa kolmesta tehtiin hapankäsittelyinä, lähtöliuoksena alumiinisulfaatti, neutraloimalla NaOH ja Na_2CO_3 seoksella toinen pH 6:een ja toinen pH 8:aan. Kolmas sarja tehtiin emäksisenä, lähtöliuoksena natriumaluminaatti, neutraloimalla H_2SO_4:lla pH 7:ään. Saostuslämpötila, neutralointikemikaalien syöttö ja pitoisuudet, suodatus- ja pesutapahtumat sekä märän kakun kuivaus, valittiin Tuomo Keskisaaren diplomityön perusteella ja ne pidettiin vakioina jokaisessa saostuksessa.

Piin läsnäolo emäksisissä yhdistelmäsaostuksissa vaikutti alumiinihydroksidin amorfisuuteen. Emäksiset saostumat, jotka eivät sisältäneet piitä, olivat kiteistä bayeriittiä tai bayeriitin ja böhmiitin seosta. Happamat saostumat olivat pseudoböhmiittiä, joko täysin amorfisia tai sisälsivät böhmiittikiteitä, AlO(OH).

Alumiinipohjaisen hydroksidien kiteisyys vaikutti saostuman moniin kemiallisiin ja fysikaalisiin ominaisuuksiin. Amorfiset saostumat olivat mm. huokoisempia kuin kidealkioita sisältäneet amorfiset tai kiteiset saostumat. Hapankäsittelyissä natrium- ja sulfaattipitoisuudet laskivat yhdistelmäsaostuksissa puhtaaseen alumiinihydroksidisaostumaan verrattuna. Natriumpitoisuudet kasvoivat ja sulfaattipitoisuudet vaihtelivat emäksisissä yhdistelmäsaostuksissa.

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1 INTRODUCTION

Titanium dioxide (TiO_2) is the most important white pigment. Titanium dioxide pigment has gained popularity due to its optical properties. In addition, good dispersibility, dispersion stability and exterior durability, e.g. exceptional light- and weather resistance, are vital in various applications. Titanium dioxide pigments are produced as a form of rutile or anastase. Titanium dioxide pigments are used in multiple applications such as paints and coatings, inks, plastics, paper, cosmetic, pharmaceuticals and food market.

Sachtleben Pigments produces TiO_2 pigment via sulphate process. Sachtleben supplies both anatase and rutile titanium dioxide modifications. These white pigments are nontoxic and offer absolutely no health risks. Anatase TiO_2 is the focus of production at Duisburg, Germany. The rutile pigments produced at Pori Finland complement the Duisburg range well.

TiO_2 pigments need to be surface treated before they are used in applications. Rutile pigments have between 1 and 15 % inorganic surface treatment chemicals and anatase pigments generally have lower coating levels of 1 to 5 %. The purpose of coating is to optimize dispersibility, dispersion stability, opacity, gloss and durability of the TiO_2 pigments. The treatments are tailored to the requirements of the final application. Different combinations of surface treatment chemical allow the use of pigment in various applications.

The most important surface treatment compound is aluminium hydroxide in its various forms. In addition, the pigments are coated with other surface treatment compounds such as P_2O_5, SiO_2, soluble TiO_2 and ZrO_2. Both basic and acidic alumina surface treatments are used in Sachtleben Pigments' pigment process.

The present work focused on precipitations of differently mixed surface treatment chemicals. Instead of performing these surface treatments on pigments, it was choicen to precipitate pure surface treatments with different combinations. The aim of the work was to examine other surface treatment chemicals' effect on alumina's properties. The precipitations prepared were basic and acidic based. The precipitation parameters were constant and were chosen according to master's thesis of pure alumina precipitation carried out by Tuomo Keskisaari.

2 PRODUCTION OF TITANIUM DIOXIDE PIGMENTS

Chemically, titanium white is titanium dioxide either in an anatase or rutile form. There is a third crystalline form, brookite, which has no commercial importance. The history of this pigment is relatively short compared to other white pigments. Commercial production of this pigment was discovered during century 1900 in Norway and in the United States. These investigations were focused in converting ilmenite to iron or titanium–iron alloys. The first industrial productions of titanium white were reported in 1918 in Norway, the United States, and Germany. These processes were not producing pure titanium dioxide as a white pigment, but as a mixture with barium sulfate. The first manufacturing of pure titanium white for pigment use (anatase form) was reported in 1923 in France. However, the real growth of the production and use of titanium white pigments began in the early 1930s and continued today, altought the rate of growth has decreased recently. /1/

Titanium white pigments are commercially produced either by the older sulphate process (SP), or by the chloride processes (CP). The advantages of the sulphate process are low capital investment and low energy consumption. The disadvantage is the formation of a large amount of by-products: 3–4 tons of ferrous sulphate heptahydrate $FeSO_4 \cdot 7H_2O$ and 8 tons of diluted sulphuric acid for each ton of titanium dioxide pigment. The chloride process is simple, but requires more expensive raw materials and higher capital investment. /1/

2.1 Sulphate Process

The name of the sulphate process comes from the dissolving of titanium raw material in sulphuric acid. The sulphate process is a batch, or discontinuous, process utilising a large number of relatively simple unit operations. In sequence, the primary unit operations are

- Digestion—reaction of a containing mineral TiO_2 and sulphuric acid. Titanyl sulphate is formed. The following reaction takes place in this first step:

$$FeOTiO_2 + 2\ H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2\ H_2O \qquad (1)$$

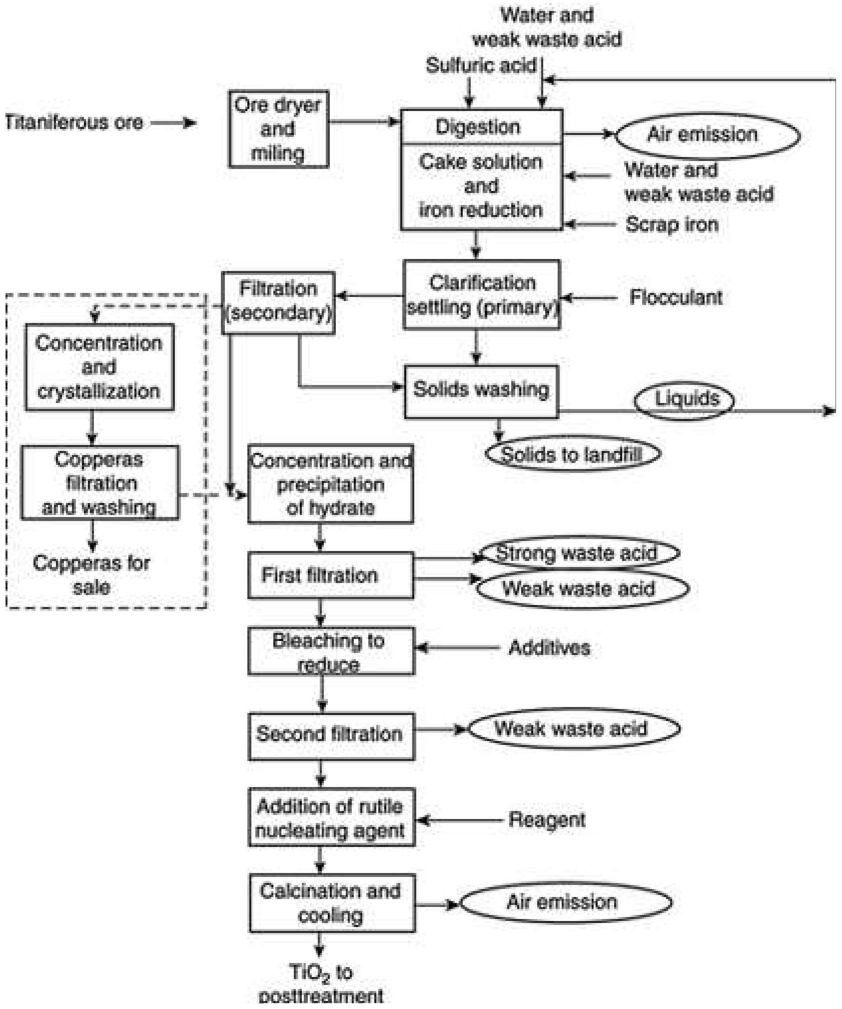
- Precipitation of titanium dioxide hydrate:

$$TiOSO_4 + 2\ H_2O \rightarrow TiO(OH)_2 + H_2SO_4 \qquad (2)$$

- Separation and washing of the hydrate
- Calcination—thermal formation of pure TiO_2 crystals:

$$TiO(OH)_2 \rightarrow TiO_2 + H_2O \qquad (3)$$

At this point, the TiO_2 product is chemically, but not physically, suited to function as a pigment, because of its large calcined particle size and far-from-uniform particle size distribution. Subsequent processing steps are needed to mill or grind the particles and disperse them to a suitable particle size to function as a pigment, and to add chemicals to the surface of the pigment particles that enhance the optical and physical properties of the TiO_2 pigment. These process steps are collectively referred to as surface treatment and are similar for both the sulphate and chloride processes. /1/



Picture 1 Sulphate process of TiO2 pigment manufacture /1/

2.2 Finishing of TiO_2 Pigments

Rutile pigments produced by the chloride and sulphate routes are basically similar and require coating for the same reasons, i.e., to optimise dispersibility, dispersion stability, opacity, gloss and durability. The coating techniques are essentially common to sulphate and chloride-route base pigments. Because the treatments are tailored to the requirements of the final application, the details are specific to the needs of the different market sectors, e.g., paints, plastics, and paper. Rutile pigments have between 1 % and 15 % inorganic coating, the higher coating levels typically used for applications such as matte emulsion paints. Anatase pigments generally have lower coating levels, of 1- 5 %. The first finishing stage is to disperse the base pigment in water, generally with phosphate, silicate, and/or organic additives. The resulting suspensions may then be milled and/or classified to remove oversize particles. The dispersed particles are then surface treated by selective precipitation of (usually) small quantities of colourless hydrous oxides, e.g., phosphorus, silicon, aluminium, titanium and zirconium deposited via controlled changes in pH and temperature. The detailed chemistry to ensure that deposition occurs on the pigment surface and not as a bulk precipitate is more complex and not completely understood. /2/

After the surface treatment stage, the pigment that has, perforce, flocculated during the treatment process, is filtered, washed, and dried. It is then milled once more, usually in a steam-fluid-energy mill (micronizer) to break up the flocculates. At the same time, the pigment is surface treated with an organic additive, e.g., polyol or alkanolamine, which are designed for use in paints and printing inks, or siloxane on pigments for plastics. Finally, the pigment is packed. /2/

3 ALUMINIUM

The atomic number for aluminium is 13 and its atomic weight is 26.981 g/mol. It is the third most abundant element in the earth’s crust. The ground state distribution of electrons in the aluminium atom is $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminium occurs in hydroxide, oxide–hydroxide, fluoride, sulphite, or phosphate compounds in a large variety of minerals and ores. /3/

The oxidation state of aluminium is +3, except at high temperatures where monovalent species such as AlCl, AlF, and Al_2O have been spectrally identified. At lower temperatures, these compounds disproportionate

$$3Al_2O \rightarrow Al_2O_3 + 4Al \qquad (4)$$

There is much discussion on the nature of the aluminium species present in slightly acidic and basic solutions. There is general agreement that in solutions below pH 4, the mononuclear Al^{3+} exists coordinated by six water molecules, i.e. $[Al(H_2O)_6]^{3+}$. The strong positive charge of the Al^{3+} ion polarises each water molecule and as the pH is increased, a proton is eventually released, forming the monomeric complex ion $[Al(OH)(H_2O)_5]^{2+}$. At about pH 5, this complex ion and the hexahydrated Al^{3+} are in equal abundance. The pent hydrate complex ion may dimerise by losing two water molecules

$$2[Al(OH)(H_2O)_5]^{2+} \rightarrow [Al_2(OH)_2(H_2O)_8]^{4+} + 2H_2O \qquad (5)$$

Further deprotonation, dehydration, and polymerization of monomers and dimers may yield ring-like structures of hydroxyl–aluminium complexes. Coalescence of ring compounds into layers by further growth results in the formation of crystalline aluminium hydroxide at pH 6, the point of minimum aqueous solubility. /3/

Aluminium hydroxide is capable of reacting as either an acid or a base.

$$Al(OH)_3(s) \rightarrow Al^{3+} + 3OH^- \qquad (6)$$

$$Al(OH)_3(s) \rightarrow AlO_2^- + H^+ + H_2O \qquad (7)$$

and the hydroxide is readily soluble, both in acids and in strong bases

$$Al(OH)_3 + 3H^+ + 3H_2O \rightarrow [Al(H_2O)_6]^{3+} \qquad (8)$$

$$Al(OH)_3 + OH^- + 2H_2O \rightarrow [Al(OH)_4(H_2O)_2]^- \qquad (9)$$

Calcined alumina, α-Al_2O_3, and naturally-occurring corundum are practically insoluble in acids and bases, but partially calcined and low-temperature amorphous oxide, such as that which forms on nascent commercial aluminium surfaces, is soluble

$$Al_2O_3 + 6H_3O^+ + 3H_2O \rightarrow 2[Al(H_2O)_6]^{3+} \qquad (10)$$

$$Al_2O_3 + 2OH^- + 7H_2O \rightarrow 2[Al(OH)_4(H_2O)_2]^- \qquad (11)$$

The amphoteric nature of the oxide is illustrated by its ability to form silicates and aluminates in the dry state at elevated temperatures

$$Al_2O_3 + 3SiO_2 \rightarrow Al_2(SiO_3)_3 \qquad (12)$$

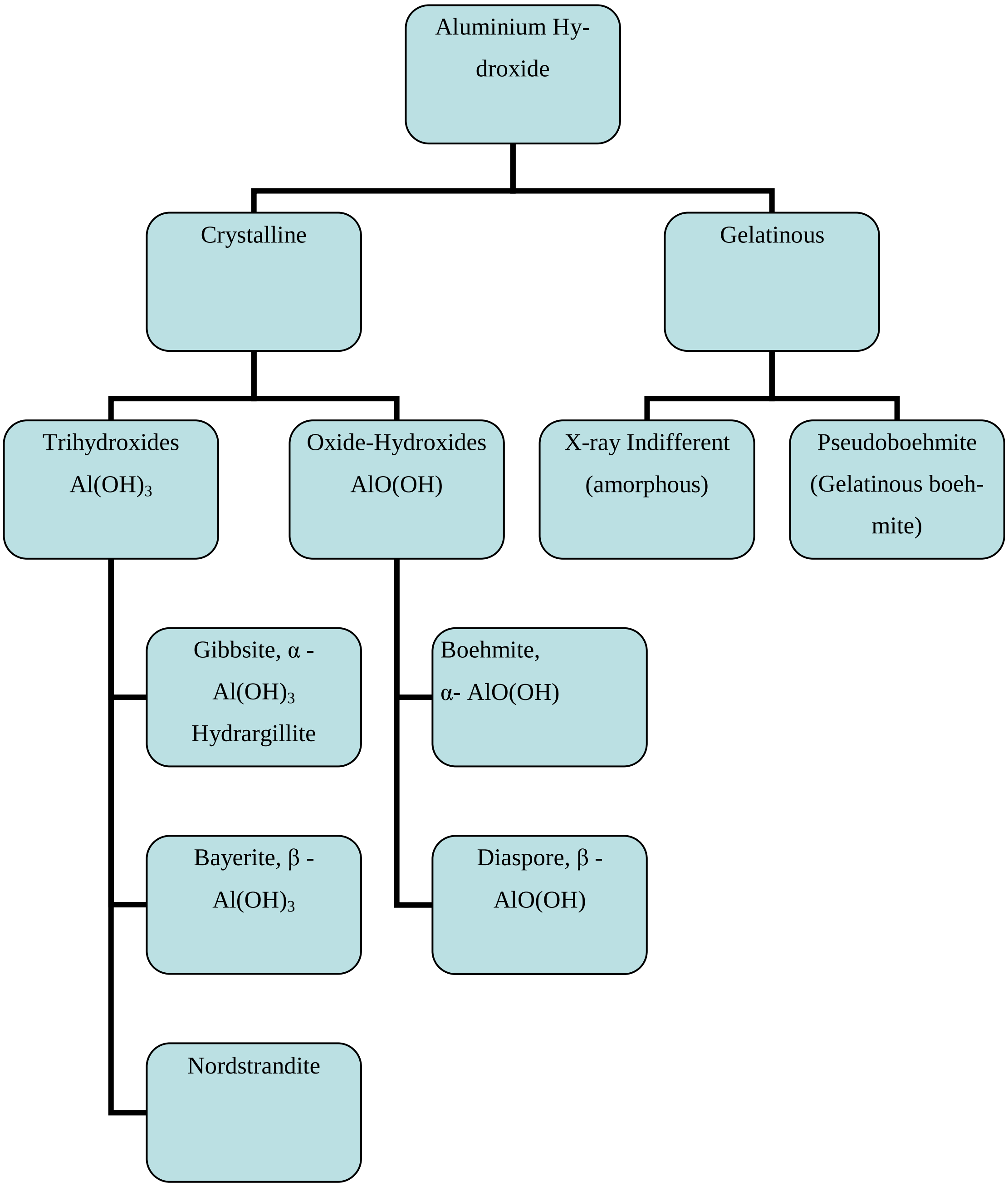
$$Al_2O_3 + CaO \rightarrow Ca(AlO_2)_2 \qquad (13)$$

Aluminium compounds, particularly the hydroxides and oxides, are very versatile. Their properties range from a hardness indicative of sapphire and corundum to a softness similar to that of talc, and from inertness to marked reactivity. /3/

3.1 Aluminium Hydroxides

The terms *alumina hydrates* or *hydrated alumina* are used in industry and commerce to designate aluminium hydroxides. These compounds are true hydroxides and do not contain hydration water. Several forms are known; a general classification is shown in Picture 2. The most well-defined crystalline forms are the trihydroxides, $Al(OH)_3$: gibbsite, bayerite, and nordstrandite. In addition, two aluminium oxide–hydroxides, AlO(OH), boehmite and diaspore, have been clearly defined. /4/

The terms *gelatinous alumina* or *alumina gel* cover a range of products in which colloidal hydrated alumina is the predominant solid phase. Structural order varies from X-ray indifferent (amorphous) to some degree of crystallinity. The latter product has been named pseudoboehmite or gelatinous boehmite. Its X-ray diffraction pattern shows broad bands that coincide with the strong reflections of the well-crystallised boehmite. /4/



Picture 2 Classification of aluminium hydroxides

3.1.1 Gibbsite

Gibbsite, (α-Aluminium Trihydroxide, Hydrargillite), commonly associated with bauxite deposits of tropical regions, is the most important aluminium compound. The gibbsite lattice consists of double layers of hydroxide ions, and aluminium occupies two-thirds of the interstices within the layers. The particle size of gibbsite varies from 0.5 mm to nearly 200 mm, depending on the method of preparation. The smaller crystals are composed of plates and prisms whereas the larger particles appear as agglomerates of tabular and prismatic crystals. The basic crystal habit is pseudo-hexagonal tabular. The usual commercial preparation method of gibbsite is by crystallisation from a supersaturated caustic aluminate, $NaAlO_2$, solution. Seed gibbsite crystals are used. /4/

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH \tag{14}$$

Crystallisation at temperatures of about 40 °C results in heavy nucleation and a fine product. At temperatures above 75 °C, only crystal growth occurs, giving rise to large, well-crystallised aggregates composed of hexagonal rods and prisms. Gibbsite usually contains several tenths of a percent of alkali metal ions; the technical product, precipitated from a sodium aluminate solution, contains up to 0.3 % Na_2O which cannot be washed out even using dilute HCl. /4/

3.1.2 Bayerite

Bayerite, β-Aluminium Trihydroxide, is rarely found in nature. It has been synthesised by several methods: A pure product is prepared by the Schmäh method in which amalgamated aluminium reacts with water at room temperature. Other methods include rapid precipitation from sodium aluminate solution by CO_2 gas, aging of gels produced by neutralisation of aluminium salts with NH_4OH, and rehydration of transition rho alumina. Unlike gibbsite, pure bayerite can be prepared with no alkali ions and there is evidence that bayerite converts irreversibly to gibbsite in the presence of alkali (Na and K) metal ions. Bayerite does not form well-defined single crystals for proper structural analysis. The most commonly observed growth forms are spindle or hourglass shapes formed by stacking of $Al(OH)_3$ layers in a direction perpendicular to the basal plane. The bayerite lattice is also composed of double layers of OH, but hydroxyl groups of one layer lie in the depressions between the OH positions of the second. These approximately hexagonal close packing results in the higher density of bayerite compared to that of gibbsite. /4/

3.1.3 Nordstrandite

The X-ray diffraction pattern of an aluminium trihydroxide which differed from the patterns of gibbsite and bayerite was published prior to the neither material, named nordstrandite, being found in nature. The nordstrandite structure is also assumed to consist of double layers of hydroxyl ions, and aluminium occupies two-thirds of the octahedral interstices. Two double layers are stacked in the gibbsite sequence followed by two double layers in the bayerite sequence. /4/

3.1.4 Boehmite

Boehmite, the main constituent of bauxite deposits in Europe, is also found associated with gibbsite in tropical bauxites in Africa, Asia, and Australia. Hydrothermal transformation of gibbsite at temperatures above 150 °C is a common method for the synthesis of well-crystallised boehmite. Higher temperatures and the presence of alkali increase the rate of transformation. Boehmite crystals of 5–10 mm are produced by this method. Fibrous (acicular) boehmite is obtained under acidic hydrothermal conditions. Excess water, about 1 % to 2 % higher than the stoichiometric 15 %, is usually found in hydrothermally-produced boehmite. /4/

The structure of boehmite consists of double layers, in which the oxygen ions exhibit cubic packing. Hydroxyl ions of one double layer are located over the depression between OH ions in the adjacent layer such that the double layersare linked by hydrogen bonds between hydroxyls in neighbouring planes. There is some technical production and use of synthetically produced boehmite. /4/

3.1.5 Diaspore

Diaspore, β-Aluminium Oxide Hydroxide, found in bauxites of Greece, China, and Russian, can also be obtained by hydrothermal transformation of gibbsite and boehmite. Higher (>200 °C) temperatures and pressure (>15 MPa-150 bar) are required for synthesis and the presence of diaspore seed crystals helps to avoid boehmite formation. In the diaspore structure, the oxygen ions are nearly equivalent, each being joined to another by way of a hydrogen ion and arranged in hexagonal close packing. This arrangement accounts for the higher density of diaspore as compared to boehmite. Although diaspore-containing bauxites and clays have been used for the production of high alumina refractories, no commercial use or large-scale synthesis of diaspore has been reported. /4/

3.1.6 Gelatinous Aluminium Hydroxides

Apart from the crystalline forms, aluminium hydroxide often forms a gel. Fresh gels are usually amorphous, but crystallise on aging, and gel composition and properties depend largely on the method of preparation. Gel products have considerable technical use.

Aluminium hydroxide gels contain considerable excess water and variable amounts of anions. Even after prolonged drying at 100 –110 °C, the water content can be as high as 5 mol H_2O/mol Al_2O_3. The initial precipitated product is usually amorphous (X-ray indifferent), except for material prepared at a pH above 7 or at high temperatures. Gradual transformation to crystalline hydroxide (aging) occurs; the rate is dependent on the OH ion concentration and temperature. Gelatinous boehmite is the first X-ray identifiable crystalline phase and the diffraction pattern shows broad bands that coincide with strong reflections of well-crystallised boehmite. In contact with mother liquor having a pH greater than 7, gelatinous boehmite transforms into crystalline trihydroxides; the rate of transformation increases with an increased pH and temperature. The transformation sequence may be represented by

$$Al^{3+} + 3OH \xrightarrow{pH<8} basic\ Al^{3+} salt^{pH\,8} x - ray\ amorpousegel^{pH\,9} gelantinous\ boehmite$$

$$\xrightarrow{pH10} bayerite\ (ortnordstrandite) \xrightarrow{+Na^{+} or K^{+}} gibbsite$$

/4/

4 TITANIUM

Titanium, Ti, is the ninth most common element in the earth's crust (ca 0.6 % by weight) and is widely distributed. Titanium's atomic number is 22 and its relative atomic mass is 47.90 g/mol. It is found particularly in rutile ores, TiO_2, and ilmenite, $FeTiO_3$. Its technologically important chemistry is predominantly that of oxidation states (II), (III), and (IV), in order of increasing importance. Ti(II) and Ti(III) compounds are readily oxidised to the tetravalent state by air, water, and other oxidising agents. The titanium compounds of greatest technological importance are titanium dioxide, the predominant white pigment. /5/

4.1 Hydrated Titanium Oxides

Hydrolysis of solutions of Ti(IV) salts leads to precipitation of a hydrated titanium dioxide. The composition and properties of this product depend critically on the precipitation conditions, including the reactant concentration, temperature, pH, and choice of the salt. At room temperature, a voluminous and gelatinous precipitate forms. This has been referred to as orthotitanic acid and has been represented by the nominal formula $TiO_2 \cdot 2H_2O$ ($Ti(OH)_4$). The gelatinous precipitate either redissolves or peptises to a colloidal suspension in dilute hydrochloric or nitric acid. If the suspension is boiled, or if precipitation is from hot solutions, a less-hydrated oxide forms. This has been referred to as metatitanic acid, nominal formula $TiO_2 \cdot H_2O$ ($TiO(OH)_2$). /5/

5 PHOSPHORUS

Phosphorus is a non-metallic element having widespread occurrence in nature as phosphate compounds. Fluorapatite $Ca_5F(PO_4)_3$, is the primary mineral in phosphate rock ores from which useful phosphorus compounds are produced. Elemental phosphorus is produced and marketed in the a-form of white or yellow phosphorus, the tetrahedral P_4 allotrope. A small amount of red amorphous phosphorus, P, is produced by conversion from white phosphorus. White phosphorus as the element is characterised by its combustion in air to form phosphorus pent oxide. /6/

Phosphorus shows a range of oxidation states from -3 to +5 by virtue of its electronic configuration. Elemental P_4 is oxidised easily by non-metals such as oxygen, sulphur, and halides to form compounds such as P_2O_5, P_2S_5, and PCl_3. /6/

5.1 Phosphorus Pent Oxide

Because of the high stability of the P–O and P— O bonds, the largest group of phosphorus compounds is the oxides. There are five well-defined oxides of phosphorus: phosphorus (III) oxide, P_4O_6, phosphorus (V) oxide (phosphorus pent oxide), P_4O_{10}, phosphorus tetroxide P_2O_4, tetra phosphorus heptoxide, P_4O_7, and tetra phosphorus nonaoxide, P_4O_9. All are obtained by direct oxidation of phosphorus. The structures of P_4O_6 and P_4O_{10} are related to that of the phosphorus molecule. /6/

6 ZIRCONIUM

Zirconium is classified in subgroup IVB of the periodic table with its sister metallic elements titanium and hafnium. Zirconium forms a very stable oxide. The principal valence state of zirconium is +4, its only stable valence in aqueous solutions. Zirconium occurs naturally as a silicate in zircon, the oxide baddeleyite and in other oxide compounds. Zirconium is an almost ubiquitous mineral, occurring in granular limestone, gneiss, syenite, granite, sandstone, and many other minerals, albeit in small amounts, so that zirconium is widely distributed in the earth’s crust. The average concentration of zirconium in the earth’s crust is estimated at 220 ppm. /7/

Zirconium is a hard, shiny, ductile metal, similar to stainless steel in appearance. It can be hot-worked to form slabs, rods, and discs from arc-melted ingot. Further cold-working of zirconium with intermediate annealing produces sheets, foil, bar wire, and tubing. Zirconium forms anhydrous compounds in which its valence may be 1, 2, 3, or 4, but the chemistry of zirconium is characterised by the difficulty of reduction to oxidation states less than four. Zirconium is a highly active metal which, like aluminium, seems quite passive because of its stable, cohesive, protective oxide film which is always present in air or water. /7/

6.1 Hydrous Oxides and Hydroxides of Zirconium

Zirconium dioxide, ZrO_2, is the most important oxide of zirconium. In its pure state it exists in four solid phases: monoclinic, tetragonal, orthorhombic, and a cubic fluorite structure. The monoclinic phase is stable up to approx. 1100 °C, and transforms to tetragonal as the temperature increases to 1200 °C. Zirconium oxide is stable to most reagents but dissolves slowly in hot concentrated sulphuric acid and in concentrated hydrofluoric acid. /7/

Hydroxide addition to aqueous zirconium solutions precipitates a white gel formerly called a hydroxide, but now commonly considered hydrous zirconium oxide hydrate, ZrO_2*nH_2O. However, the behaviour of this material changes with time and temperature. The hydroxides as precipitated are amorphous, but if they are refluxed in a neutral or slightly acidic solution they convert to a mixture of cubic and monoclinic hydrous zirconia crystallites; on continued refluxing, only the monoclinic form persists. If the refluxing is conducted in an alkaline solution, metastable cubic zirconia is formed. /7/

Phosphate ions precipitate group IVB metals from strong acid solutions. This ability is used in analytical procedures to separate zirconium from other elements, and to prepare zirconium phosphates. The precipitate is a gelatinous amorphous solid of variable composition. However, when refluxed in strong phosphoric acid, a crystalline, stoichiometrically constant compound forms with a composition of $Zr(HPO_4)_2*H_2O$, known as zirconium bis(monohydrogen phosphate) or a zirconium phosphate. /7/

7 SILICON

Silicon occurs naturally in the form of oxides and silicates and constitutes over 25% of the earth's crust. More than half of the elements in the Periodic Table react with silicon to form one or more silicides. /8/

7.1 Silicon Dioxide

Silica and silicates in the form of amorphous white powders can also be made synthetically, using a thermal or pyrogenic process (fumed silica) or a wet process (precipitated silica, silica gels). Amorphous silica is used in various industries, such as food, animal feed, personal care, paper, tyres, plant protection and numerous others, and is an essential part of many everyday products. The thermal process leads to fumed silica, the wet process to either precipitated silica or silica gels. /8/

The raw materials used for the production of precipitated silica are alkali silicate solutions, preferably sodium silicate and acid. Typically, precipitated silica is manufactured at pH values >7, whereas silica gels are manufactured at pH values <7. The chemical reaction is described in the following formula. /8/

$$Na_2O \cdot 3.3\, SiO_2 + H_2SO_4 \rightarrow 3.3\, SiO_2 + Na_2SO_4 + H_2O \qquad (15)$$

After the chemical reaction (precipitation) has been completed, the suspension obtained is filtered, and the filter cake is washed to remove the sodium sulphate. Depending on the drying technology and the required particle size of the silica, the product can be optionally milled to obtain a finer particle size or granulated to convert the powder into a low dust form. /8/

The specific surface of silica is generally determined using the Brunauer-Emmett-Teller (BET) adsorption method or a modification thereof. The BET surface always provides the sum of the so-called outer geometrical surface and the inner surface, ie, the surface within the porous structure of the silica. Synthetic silica is amorphous: that is, unlike crystalline solids, silica does not possess an infinite three-dimensional long-range order. Loss in drying and loss on ignition are significant characteristic parameters that can be used to characterise the differences between synthetic silica. Precipitated silica and silica gels typically exhibit a loss on ignition of more than 3% (typically in the region of 5 %), provided they have not received special after treatment. /8/

The increasing demand for matte-finish paint systems led to an increasing demand for silica. Changing trends in coatings technology have forced many formulators to re-examine their requirements for the performance of matting agents. As the industry moves from conventional solvent-based systems to high solid and water based technology, the matting performance of the agents becomes more critical for uniform and consistently matte finishes. Fumed, precipitated silica, and silica gel vary in average particle size, particle size distribution, oil absorption, moisture content and surface treatment. All of these characteristics play an important role in how well the matting agent will perform in each system. The formation of a coating film surface with defined roughness, and hence the degree of matting, can be influenced by changing the characteristics of the silica. /8/

8 BACKGROUND AND GOAL OF THE WORK

According to literature and previous studies, many factors influence the properties of alumina-based precipitations. The purpose of this work was to study the behaviour of various combinations of surface-treatment chemicals on TiO_2 pigments in alumina-based precipitations. The results of these studies can be utilised in surface treatment studies of TiO_2 pigments.

8.1 Previous Studies on Alumina Precipitations

This work was based on a previous study of pure alumina precipitations carried out by Tuomo Keskisaari. According to Tuomo Keskisaari's Master's thesis the precipitation process has a significant influence on the properties of alumina.

Wet aluminium hydroxide precipitates prepared from an acidic precursor contained more moisture, sulphates and sodium than did those from basic precursor. The alumina powders prepared from the acidic sulphate precursor were predominantly of the pseudoboehmite phase after drying, but the level of crystallinity varied between amorphous and crystalline. /18/

The basic precipitation led the alumina in the form of crystalline bayerite with lower amounts of moisture and sulphates present, irrespective of the choice of the different parameters. In the case of the acidic precipitation, high pH and high concentration of precipitant gave the alumina an increased level of crystallinity and Al_2O_3 content. /18/

Generally, the properties of bayerites were uniform but those of pseudoboehmites varied markedly.

The acidic precipitation led to higher specific surface areas and pore volumes of alumina powder than did the basic precipitation. Crystalline boehmites have very high surface areas and pore volumes. Acidic precipitation gave alumina higher brightness and lower tone values than basic precipitation unless they were crystalline, or soda had been used. Drying in a rotating tube furnace had a favourable effect in respect of increased level of crystallinity and decreased amount of moisture, compared to drying in an air circulation drying oven. /18/

8.2 Background and Goals of this Thesis

In this thesis, other surface treatment chemicals were studied in addition to aluminium. The chemical combinations chosen, consisted of titanium, zirconium, phosphorous and silicon-based surface-treatment chemicals, which are used in surface treatment formulations of TiO_2 pigments. The main aim was to compare the effect of the chemicals selected on the properties of alumina-based precipitations.

The parameters of the precipitations and the sample preparation methods were chosen according to the previous experimental study of Tuomo Keskisaari. The amounts of other chemicals were chosen so that they synchronised with their amounts in the authentic TiO_2 surface treatment formulations.

Since in the previous study, the end pH of the acidic precipitations had a significant effect on the properties of alumina, two different end pH values were studied - pH 6 and 8. The end pH of the basic precipitations had no effect on the results, therefore only end pH 7 was used./18/

The concentration of the precipitant and the $NaOH/Na_2CO_3$ ratio was chosen so that an amorphous precipitation could be achieved as a result of the acidic precipitations.

The temperature and the feed rate of the precipitants were kept constant. The filtration and washing methods were standardised. Only one drying method was used in order to reduce the number of parameters. The samples were analysed using the appropriate standard procedures of Sachtleben Pigments.

9 WORKING PROCEDURES

The working procedures were based on the methods developed in previous studies.

9.1 Precipitation Chemicals

In this work five different surface treatment chemicals were used:

- Aluminium used as aluminium sulphate [$Al_2(SO_4)_3$] or Sodium aluminate ($NaAlO_2$)
- Titanium used as titanyl sulphate ($TiOSO_4$)
- Silicon used as water glass (Na_2O*3.3 SiO_2)
- Phosphorus used as calgon [$(NaPO_3)_6$]
- Zirconium used as zirconium sulphate [$Zr(SO_4)_2 4H_2O$]

The same chemicals are used as surface treatments chemicals in Sachtleben Pigments' TiO_2 grades. Aluminium was prepared as 100 % aluminium hydroxide given as Al_2O_3. Each other chemical was added into the aluminium solutions as such or in combination together with other surface treatment solution(s). These samples included 80 % aluminium hydroxide given as aluminium oxide and 20 % other surface treatment chemicals given as oxide (Table 1).

Table 1 Keys to precipitation numbers

	/1	**/2**	**/3**	**/4**	**/5**	**/6**	**/7**	**/8**	**/9**	**/10**	**/11**	**/12**
Surface Treatment Chemicals Added [%]	Al_2O_3 100 %	Al_2O_3 80 % TiO_2 20 %	Al_2O_3 80 % P_2O_5 20 %	Al_2O_3 80 % ZrO_2 20 %	Al_2O_3 80 % SiO_2 20 %	Al_2O_3 80 % TiO_2 15 % P_2O_5 5 %	Al_2O_3 80 % TiO_2 15 % ZrO_2 5 %	Al_2O_3 80 % ZrO_2 10 % P_2O_5 10 %	Al_2O_3 80 % TiO_2 10 % ZrO_2 5 % P_2O_5 5 %	Al_2O_3 80 % SiO_2 10 % P_2O_5 10 %	Al_2O_3 80 % SiO_2 10 % ZrO_2 10 %	Al_2O_3 80 % SiO_2 10 % ZrO_2 5 % P_2O_5 5 %

All chemicals except sodium aluminate were taken from Sachtleben Pigments' plant. Due to the instability of sodium aluminate, it was prepared in the laboratory a day before each basic precipitation. Large volumes of the solutions were delivered at the same time to maintain consistent quality. All chemicals concentrations brought from the plant were checked by the factory's own maintenance system (Lims) and analysed in the laboratory (Table 2).

Table 2 Oxide concentrations of chemicals used

	Oxide concentration by Lims [g/l]	**Analysed oxide concentration [g/l]**
Aluminium sulphate	76.6	77.4
Sodium aluminate	made in laboratory	73.2
Titanyl sulphate	76.2	76.2
Water glass	68.0	68.0
Calgon	102.2	98.9
Zirconium sulphate	187.7	184.0

9.2 Precipitant Chemicals

The following precipitant chemicals were used:

- Sodium hydroxide (NaOH)
- Sodium carbonate (Na_2CO_3)
- Sulphuric acid (H_2SO_4)

Large volumes of the solutions were delivered at the same time to maintain consistent quality. Additional precipitants were required. The precipitant chemicals NaOH and Na_2CO_3 were diluted in the laboratory and mixed together at a mole ration of 9:1 before usage.

9.3 Precipitation Series

Three different precipitation series were prepared. Two precipitation series were based on acidic aluminium sulphate, and the third series was based on basic sodium aluminate. The acidic precipitations were neutralised up to pH 6 (code MM1A) and pH 8 (code MM1B). The basic precipitation was neutralised down to pH 7 (code MM2). Each series included twelve samples. All precipitations were prepared once, with the exception of precipitation MM2/2, which was prepared twice. In addition, one single reference precipitation (code MM0B) was prepared. Four different types of precipitant were used (Table 3).

T**able 3** Key to precipitation codes

Code	Main Precipitation Chemical	Precipitant	End pH
MM0B (Reference)	Acidic aluminium sulphate	NaOH, 300 g/l	8
MM1A	Acidic aluminium sulphate	NaOH, 200 g/l and Na_2CO_3, 150 g/l (mole ration 9:1)	6
MM1B	Acidic aluminium sulphate	NaOH, 200 g/l and Na_2CO_3, 150 g/l (mole ration 9:1)	8
MM2	Basic sodium aluminate	Sulphuric acid, 300 g/l (H_2SO_4)	7

9.3.1 Preparation of Sodium Aluminate Solution

Sodium aluminate was prepared in the laboratory a day before usage. The solution was prepared in a ten (10)-litre round-bottomed flask. The flask was put into a heated bath (Isopad) with a mechanical agitator (Heidolph) and a digital thermometer (Isopad TD2000). An amount of 5.5 litres of solution was prepared at the time. An amount of 517 g analytical reagent grade granules of NaOH was weighted with 660 ml cold TS-water into the flask. After the solution had become clear, 660 g aluminium trihydroxide was added slowly over a 20-minute time period. The slurry was then heated to 115 °C and cooled in air to below 100 °C. Finally the solution was diluted at room temperature with TS-water to a volume of 5.5 litres. After the first solution preparation the solution was analysed in the process laboratory (Table 2). It was assumed that all sodium aluminates solutions were identical.

9.3.2 Preparation of Precipitant Solutions

The same sulphuric acid as used in the surface treatment of Sachtleben Pigments was used in the basic precipitations. Its concentration was 321 g/l.

NaOH and Na_2CO_3 solutions, which were used in the acidic precipitations, were also brought from the plant. Sodium hydroxide was diluted from a concentration of 300 g/l to 200 g/l and sodium carbonate was diluted from 190 g/l to 150 g/l with TS-water. After checking the concentrations, the amounts were calculated and the solutions mixed in a mole ratio of 9:1 (9 mol NaOH and 1 mol Na_2CO_3).

Diluted NaOH and Na_2CO_3 mixtures were prepared and analysed twice. The first diluted solutions had concentrations of 220 g NaOH/l and 145 g Na_2CO_3/l and the second of 217 g/l and 147 g/l, respectively (Tables 4 and 5).

Table 4 Analyses of the first precipitant solutions after diluting and mixing

Diluted solutions	**Concentration analysed [g/l]**	**Quantity of Material, n [mol]**	**Volume in mixing [ml]**	**Used on series**
1. NaOH	220	9	1640	MM1A/1-2, 1B/1-4
1. Na_2CO_3	145	1	720	MM1A/1-2, 1B/1-4

Table 5 Analyses of the second precipitant solutions after diluting and mixing

Diluted solutions	**Concentration analysed [g/l]**	**Quantity of Material, n [mol]**	**Volume in mixing [ml]**	**Used on series**
2. NaOH	217	9	1660	MM1A/3-12, 1B/5-12
2. Na_2CO_3	147	1	710	MM1A/3-12, 1B/5-12

The volumes can be calculated with the following equations

$$n = \frac{m}{M} \tag{16}$$

$$c = \frac{n}{V} \Rightarrow V = \frac{n}{c} \tag{17}$$

where
n= quantity of material, mol
m= mass, g
M= mole mass, g/l
V= volume, l
c= concentration, mol/l

The mixing ratio of the first precipitant solutions, 1.6 l: 0.7 l, was calculated with formulae (16) and (17)

$$c(NaOH) = \frac{220 g/l}{40 g/mol} = 5.5 mol/l$$

$$V(NaOH) = \frac{9 mol}{5.5 mol/l} = 1.64 l$$

$$c(Na_2CO_3) = \frac{145 g/l}{104 g/mol} = 1.39 mol/l$$

$$V(Na_2CO_3) = \frac{1 mol}{1.39 mol/l} = 0.72 l$$

The other precipitant solutions diluted and analysed were calculated in a similar way.

One single precipitation, MM0B with aluminium sulphate, was also prepared. In this case the precipitant used was NaOH with a concentration of 300 g/l. This concentration is the same as that used in the pigment production process and also in Tuomo Keskisaari’s thesis.

9.4 Precipitation Equipments and Arrangements

Experimental arrangements included ten-litre round-bottomed flasks with a heated bath. There was also a mechanical agitator (Heidolph), a digital thermometer (Isopad

TD2000), pH meter (Schott Handylab ph meter) for measuring pH, a stopwatch for timekeeping and an automatic feeding pump (Masterflex L/S Economy Drive) (Picture 3).

The precipitation chemical solution/s was/were poured into the flask and was/were heated to 50 °C. A suitable rate of stirring was set and it was continuous throughout. Precipitant feed was started with an automatic feeding pump with silicon hoses. The feeding rate was set to 40 ml/min. Timekeeping was started simultaneously with the feeding.

Picture 3 The experimental arrangements of the precipitations

9.5 Working Procedures of Acidic Precipitations

Twenty five different precipitations based on acidic aluminium sulphate were prepared. These series were coded as MM1A/1-12 (to end pH 6), MM1B/1-12 (to end pH 8) and the single one MM0B (end pH8). The precipitant was mixed NaOH (concentration approx. 200 g/l) and Na_2CO_3 (concentration approx. 150 g/l) in a mole ration of 9:1, except the single precipitation MM0B. An amount of the treatments of 2 litres was used. The amounts of chemical addition were calculated according to the oxide concentration of the surface treatment solutions. In the first precipitation, the aluminium sulphate solution consisted of 100 % aluminium hydroxide given as Al_2O_3. Other precipitations included 80 % Al_2O_3 and 20% other surface treatment chemical hydroxides or their mixtures given as oxides (Appendix 1).

9.5.1 Course of Acidic Precipitations

Temperature, pH value and the formation of flocks were documented by the minute during the whole precipitation. A diagram was drawn to display the change of pH and temperature as a function of time. Immediately the precipitant feed was started, foam and small flocks were formed. The formation of flocks was dependent on the precipitants used. During precipitation flock formation was continuous. The precipitation reached flocculation point with the pH rising to a value of 3.75-3.85. The precipitant feeding was stopped because the precipitate formed a highly viscous slurry. For a while it was necessary to stir the solution manually. After passing the flocculation point, precipitation reached the end pH quickly. Feeding was stopped when the pH was the correct 6 or 8, depending on the series, but stirring was continued for ten minutes. The consumption of precipitant was measured.

9.5.2 Filtration and Washing Procedures

In the next step, the precipitation slurry was decanted into two filtration funnels (Picture 4). There were two different filtration papers on each funnel, one on top of the other, a Whatman 542 on top and a Whatman 602H on the bottom. When the all the water was filtrated from the cakes they were washed with 1400 ml warm (temperature approx. 50 °C) TS-water per funnel (Picture 4).

Picture 4 Two filtration funnels

The filtration cakes were collected together, slurred with 800 ml warm TS-water and left to stand for 40 minutes. Then filtration and washing were repeated to wash off most of the soluble salts in the precipitate. All filtrations and washing times were documented. The ready cake was weighted, the dry material content of the cake and the pH were analysed.

The cake was subsequently dried in an air circulation drying oven at a temperature of 160 °C for 21 hours.

9.6 Working Procedures of Basic Precipitation

The basic precipitations were based on sodium aluminate. Twelve different precipitations, coded MM2/1-12, were prepared using the end pH of 7. The sulphuric acid (H_2SO_4) concentration was 312 g/l. All together the treatments amounted to 5 litres. Volumes were calculated according to the oxide concentration in the surface treatment solutions. In the first precipitation there was 100 % aluminium hydroxide given as Al_2O_3. Other precipitations included 80 % aluminium hydroxide, given as Al_2O_3

and 20 % other surface treatment chemical hydroxides, or their mixtures, given as oxides (Appendix 1), as in the acidic precipitations.

9.6.1 Course of Basic Precipitation

The experiment arrangements included the same equipment as in the acidic precipitations. However, the precipitation itself was performed in a slightly different way. In order to avoid uncontrolled precipitate formation due to acidic chemicals, the precipitation chemicals were not added into the flask simultaneously. Firstly, sodium aluminate was put into the flask. The other precipitation chemicals were fed in to the flask by feeding pump at a rate of 40 ml/min, as was the precipitant. The acidic and basic solutions were fed by separate feeding pumps in order to avoid unwanted precipitations.

When the all the treatment solutions had been fed into the flask, an intermediate sample was taken from the precipitation solution. After that, precipitant sulphuric acid feeding was started at the same feeding rate of 40 ml/l. There was no need to pause the precipitant feeding during the precipitation because no flocculation formed. Temperature, pH and precipitation time were documented. Feeding was stopped at pH 7 and stirring was continued for ten minutes.

9.6.2 Filtration, Washing and Drying Procedures

Washing the basic precipitates was easier and quicker than that of the acidic precipitates. The slurry was decanted with one single funnel. Only one filtration and one washing step with 5.5 litres of warm TS-water was required. Filtration and washing time were documented. The ready cake was weighted and its dry material content and pH were analysed. The consumption of precipitant was measured.

The cake was subsequently dried in an air circulation drying oven at a temperature 160 °C for 21 hours (Picture 5). In addition, an intermediate sample was dried in the oven at same temperature.

Intermediate samples were analysed only to the extent of the chemical content of oxides (Appendix 5).

Picture 5 Two different basic precipitates after an air circulation drying oven with same dried method

10 ANALYSIS METHODS

Multiple chemical and physical analyses were conducted to analyse the alumina-based samples. After precipitation, filtration and washing, the dry material content and pH of the wet cake were analysed. After drying in an air-circulation oven, the following measurements were taken: moisture content, pH, specific resistance, brightness, oil absorption, XRF (UNIQUANT4), XRD, TGA, specific surface, pore volume and size, photo activity/stability, particle size of wet milled samples and surface charge (IEP).

10.1 Dry Material Content and Moisture

Dry material content and moisture content were measured with a Metter Toledo HG53 Halogen Moisture Analyzer. The measuring is based on the thermo gravimetrical principle. The halogen-radiation dehydrates the sample with a heating sensor while in-built precision scales continuously measure the weight of the sample. The solids content is the amount of sample remaining after a sample is dried to a constant weight. The solids content is expressed as a percentage by weight. Moisture, expressed as a percentage, is the opposite of the solids content.

A suitable amount of the wet cake sample to be tested was weighted onto a drying pan. The sample was dried to a constant weight at a temperature of 150 °C and after which a counting device, attached to the balance, calculated the solids content of the sample. Moisture content was measured on an oven-dried sample which had undergone heating at a temperature of 110 °C for six minutes. /9/

10.2 Measurement of pH

The pH was measured from all precipitations of all wet cakes and all oven-dried powders using Schott’s table-model pH meter. The pH meter was calibrated before each measurement series. A small piece of wet cake was placed into a beaker and some TS-water was added to achieve a suitable slurry. The pH was then measured.

Ten (10) grams of dry powder were weighted into the beaker with 90 ml deionised water. The beaker was set on magnetic stirring for a half an hour. The pH was then measured immediately.

10.3 Specific Resistance

The conductivity of the reference solutions was determined with a Knick Conductivity Meter 702. The conductivity measurement aided in the calculation of the specific resistance of the samples.

Ten (10) grams of the dried sample were measured into a 100-ml decanter glass with 50 ml deionised water. The decanter glass was placed on a hot plate and heated to boiling, and the solution was boiled for fifteen minutes. The solution was decanted into a 100-ml volumetric bottle, which was filled to 100 ml with deionised water. The solution was decanted into the beaker and measured using a calibrated conductivity meter. The result of the conductivity of the sample was given as mS. The specific resistance was obtained by dividing the value of 1000 by the conductivity value obtained (as kohmcm).

10.4 Dry Brightness and Tone

The method is applicable in the determination of dry brightness and tone by a HunterLab UltraScan Xe-colorimeter. The spectrophotometer determines the reflection spectrum of briquetted dry powder. The brightness value corresponds to the lightness of the sample. The more the sample reflects light, the brighter it is. The tone values are given as a measure of the yellow-blue tendency of the tone.

About five grams of ground sample were placed into a sample holder on a polished ceramic base. A sample briquette was pressed from the sample powder using a hydraulic press (Christensen). The compression force was 2 metric tons. The briquette surface was inspected to assure that it was smooth and unbroken. /10/

10.5 Oil Absorption

The method is based on the determination of the oil absorption of TiO_2 pigments. The same method was used in this work. Samples oil absorption is the amount of linseed oil required to wet a 100-g sample.

Five (5) grams of the mortar-ground sample powder were weighted for testing purposes at an accuracy of 0.1 g. Linseed oil was gradually added to the powder, drop by drop, from a burette. The test was complete when exactly enough linseed oil was incorporated with the powder.

The result of oil absorption was calculated by way of density and consumption of linseed oil in following way /11/

$$Oil\ Absorption = V_{Linseed\ Oil} \cdot \rho_{Lenseed\ Oil} \cdot 20 \qquad (18)$$

where

V = Consumption of Linseed Oil, ml

ρ = Density of linseed oil, g/ml

20 = Ratio 100/5 (100 g powder/5g sample analysed)

10.6 Chemical Content and X-ray Diffraction Analyses

Chemical content and the degree of crystallinity of the dried alumina samples were measured with X-ray fluorescence (XRF) and X-ray diffraction (XRD). The dried powder sample was put into a sample holder, a briquette, on a polished ceramic base. The briquette was pressed with a compression force of two metric tons, and analysed.

X-ray fluorescence was used to determine the chemical composition of the samples. The measurement was performed with a Philips PW3710 Spectrometer and the chemical composition obtained through the UNIQUANT4 program in oxide form. /12/

The XRD measurement was performed with a Philips PW3710 Spectrometer using Cu K_α radiation. Diffraction patterns were measured in a 2θ angle range of 10-70° with a 0.002° measurement increment. The diffraction patterns were analysed with an X'pert Graphics & Idenfity program using the JCPDS database. /13/

10.7 Wet Grinding and Measurement of Particle Size

A Malvern Mastersizer 2000 was used to measure the particle size and the particle size distribution.

Thirty (30) weight-% suspensions were prepared from samples of all samples except sample MM2/5 (= basic alumina-silica sample) from which only a 10 weight-% suspension could be made due to its high surface area.

Thirty (30) grams of the each sample were measured into glass jars with plastic seals and metal tops. Seventy (70) grams of TS-water and about 130 grams of zirconium beads were also added into the jars. The jars were placed onto a rotating roller. Samples were taken from the jars over a duration of four hours: after 30 minutes, after 2 hours and after 4 hours.

10.8 Specific Surface and Pore Volumes

Specific surface is the combined surface areas of the particles calculated to the mass unit. Specific surface was measured with a NOVA 3200 specific surface analyser. The analyser measurement is based on the adsorption of the gas-phased nitrogen molecule (N_2) with solid surface under the relative pressure ($P/P_\circ$). The nitrogen molecules are attached on the surface of the samples with a nitrogen layer having a thickness of one molecule. Determination is based on the so-called PET equation. Pore volume distribution was also acquired with this method. /14/

10.9 TGA Analysis

A thermogravimeter is particularly useful in studies of degradation mechanisms and thermal stability of materials. The moisture is water that has been combined with a sample by physical forces. The loss on ignition (LOI) is the amount of fixed components that can be removed by red-heating the sample. Such a component can be e.g. crystal water, residual sulphates, hydroxyl groups and combustible substances. /15/

A thermogravimeter, also known as a thermobalance, consists of scales (a microbalance), and a furnace. The specimen was placed on the scales, inside the furnace and any weight change in the sample was recorded during the temperature programme. The moisture was determined at a temperature of 110 °C and the loss of ignition was determined at temperature of 1000 °C. /15/

10.10 Photoactivity

In the photocatalytic reaction organic compounds decompose via possible intermediate products such as carbon dioxide (CO_2), by exposure to UV radiation and/or visible light. Photoactivity measures the efficiency of the photoactive reaction while photostability correspondingly measures the inefficiency. /16/

In this method isopropyl alcohol was decomposed via acetone to carbon dioxide. The decomposition of the sample and formation of CO_2 in the form of gas were observed with an FTIR spectrometer. The results were reported as the formation rate of CO_2 and acetone (mg/kg/h) (Table 6) as well as the decomposition of isopropyl alcohol and acetone first order of velocity constant. /16/

0	5	20	100	300
Superior	Excellent	Good	Average	Poor

Table 6 Estimation scale of photostability as acetone formation rate (mg/kg/h)

10.11 Surface Charge and Isoelectric Point

The determination of streaming current value by Mütek PCD 03 with pH is based on van der Waals absorption forces. The sample was placed into a plastic measurement container equipped with a piston. The container was set onto the Mütek PCD 03 and the device was turned on. There is a narrow gap between the inner wall of the container and the piston. This was where the colloid molecules absorb onto the surfaces of the container and the piston by forces of van der Waals. As the piston oscillates in the container it causes fluidic streaming which takes with it all free anti-ions and separates them from the absorbed fluid-sample. Anti-ions induce the current to the electrodes of the measurement container and the current is then directly streamed and confirmed. The generated current, the so-called streaming current value, is visible on the device screen./17/

Four (4) grams mortar-ground sample powder was placed into a decanter glass with 196 ml 0.001 M KCl. The decanter glass was set onto the magnetic mixer equipped with a pH meter. A 10-ml sample suspension was taken when the pH had been stabilised, and a measurement was carried out. After the first determination of the streaming current value of the sample, diluted hydrochloric acid (HCl) was added into the solution to alter the pH by about 0.5. The new streaming current value was measured and documented. At the end of the test the sample had an opposite charge.

By changing the pH, the surface charge changes and the isoelectric point can be discovered. IEP is the pH point where the potential value of the sample value is zero. A diagram was drawn to display the streaming current (mV) as a function of pH.

11 RESULTS

The samples were analysed using the various analysis techniques available at Sachtleben Pigments. The mixed precipitation samples were compared with precipitates of pure alumina samples. All surface treatment chemicals seemed to act differently when used alone and when used together. The analyses focused on the degree of crystallinity and on the chemical composition of the samples, e.g. their sulphate (SO_3) and sodium (Na_2O) contents. In addition, specific surface area and pore size analyses gave interesting results, as did determination of oil absorption.

11.1 Precipitation Process

During precipitations, the temperature, pH, precipitation time and consumption of precipitant were measured (Appendix 2). Intermediate samples were taken from the basic precipitations before feeding the precipitant, thus starting the neutralization. After precipitation the slurry was decanted, filtrated into a funnel/funnels, and washed. Filtration and washing times were also documented (Appendix 2). Filtration and washing were important steps in eliminating the sodium and sulphate content from the dry sample.

11.1.1 Precipitation Time and Precipitant Addition

Precipitation times and amount of precipitant used were dependent on the starting pH of the chemicals and on the target pH (Figure 1). Aluminium sulphate, titanyl sulphate and zirconium sulphate were the most acidic chemicals. Therefore their starting pH was lower compared to those of calgon and water glass, which are almost neutral chemicals. The amount of the precipitant used was in relation to the precipitation time, because the feed rate was the same in all precipitations (40 ml/min).

In the acidic precipitations the amount of precipitant used was dependent on the target pH value: when the end pH was 6, the amount of precipitant used was 1890-2730 ml, whereas the amount was 2070-2800 ml with an end pH of 8.

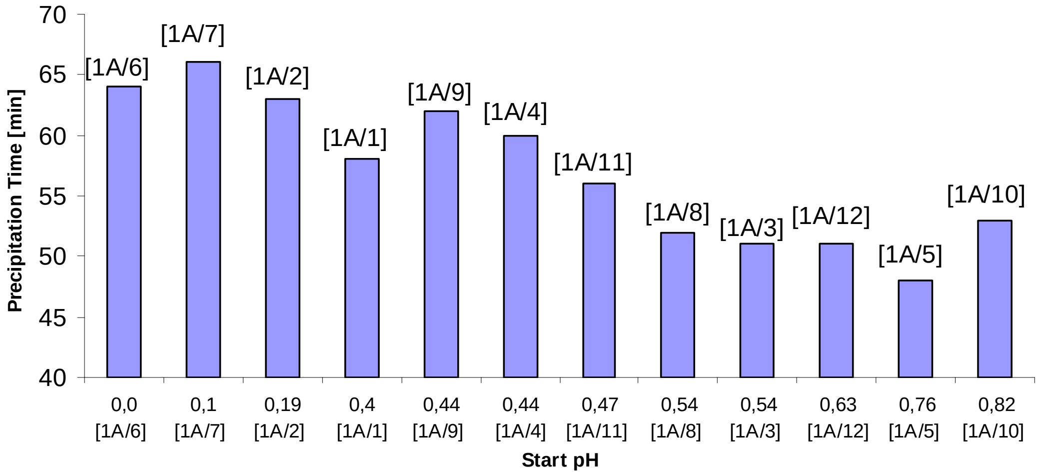


Figure 1 The precipitation time as a function of start-pH in acidic precipitations to end pH 6 (MM1A)

In basic precipitations the precipitant was added after all surface treatment chemicals had been fed. The start-pH was taken and the precipitant feed time was started at this point. The amount of precipitant used varied from 380 ml to 1600 ml. The basic precipitations actually broke a few pH meters. The conditions were so basic that the pH meter electrode had to be changed after three precipitations.

11.1.2 Temperature and pH Behaviour during Precipitations

Temperature and pH were documented during the precipitations. In all the cases the temperature behaviour was exothermic. The temperature of the warming bath could not be kept constant due to the absence of a cooling system. In all precipitations the pH value increased/decreased slowly and after reaching the equivalent point, the pH value moved quickly to the end pH.

In acidic precipitations the temperature rose at first but then stabilised. The end temperature was the same as it was at the beginning (Figure 2), which seemed to be the case in all precipitation combinations in the acidic case studies series MM1A and MM1B.

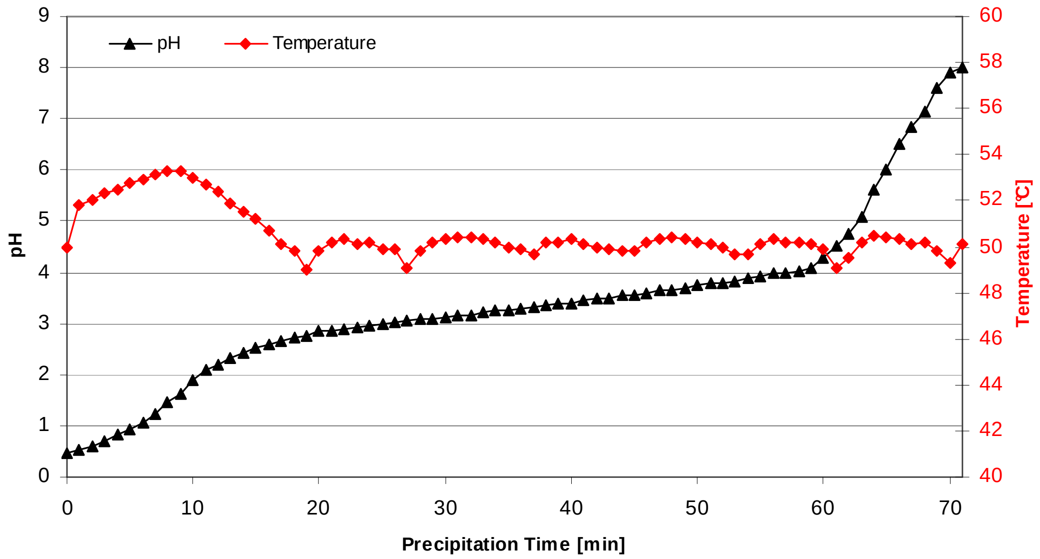


Figure 2 Temperature and pH a function of precipitation time in acidic precipitations to the end pH value of 8 (MM1B/1)

The basic precipitations proved to be exothermic reactions. The temperature rose at the beginning of the precipitant feed through to the end of the precipitations. Because of the chemical added the line did not act in a similar way at the start of each precipitation. The acidic precipitates (titanyl sulphate and zirconium sulphate) caused the temperature to increase immediately, from the start. When neutral water glass and calgon were added, the temperature remained on target until the precipitant was added. These precipitations became exothermic when sulphuric acid was added (Figure 3).

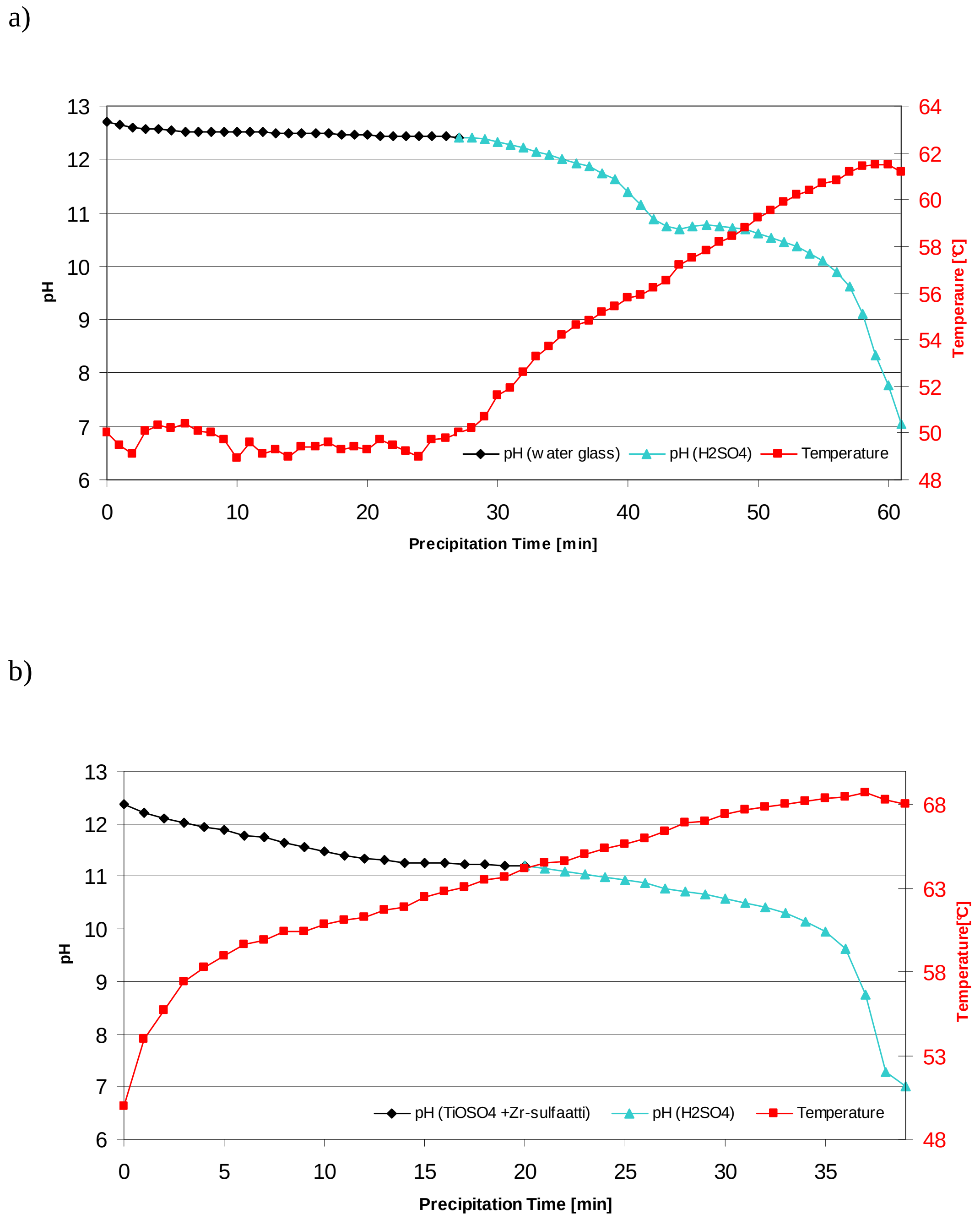


Figure 3 Temperature and pH a function of precipitation time in basic precipitations a) MM2/5 and b) MM2/7 to the end pH value of 7

In the acidic precipitations the flocculation point was reached with a pH rising to the value of 3.8 on average (Table 7). The theoretical flocculation point of aluminium is 3.8 at room temperature, 20 - 25 °C. Aluminium seemed to dominate these precipitations.

Table 7 Flocculation point of pH in acidic precipitations

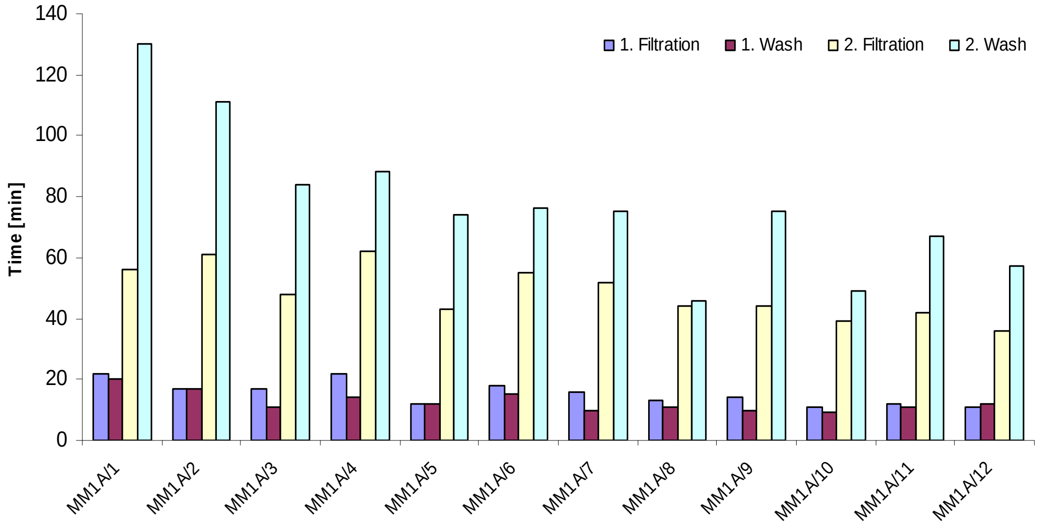
Precipitation	MM1A	MM1B
/1	4.0	4.0
/2	3.8	3.8
/3	3.7	3.7
/4	3.8	3.9
/5	3.9	3.9
/6	3.9	4.0
/7	3.9	3.9
/8	3.8	3.7
/9	3.8	3.8
/10	3.8	3.9
/11	3.9	3.9
/12	3.9	3.8
Average	**3.8**	**3.8**

11.1.3 Filtration and Washing Times of the Cakes

Filtration and washing times of the cakes varied between the acidic and basic precipitations (Appendix 2). Filtration and washing took place more quickly with the basic treatments than with the acidic ones. On the other hand, fast filtration and washing increased the sodium content of the end product.

In the acidic treatments, filtration and washing times decreased in mixed precipitations. The final pH of the precipitation affected the filtration and washing times in acidic precipitations. With an end pH value of 6, filtration and washing occurred slowly. The average time value on filtration was 15 minutes and on washing 60 minutes. In both cases the second filtration and washing took more time than first ones (Figure 4). With an end pH value of 8, filtration and washing times were on average 10 minutes and 40 minutes (Figure 4).

The basic precipitation cakes were washed only once. Filtration and washing proceeded smoothly, but left more sodium in the end product. Three precipitations contained phosphorus as Calgon -MM2/3, MM2/6 and MM2/8- were exceptions. In these three cases the washing times were long and drawn out (Figure 5).



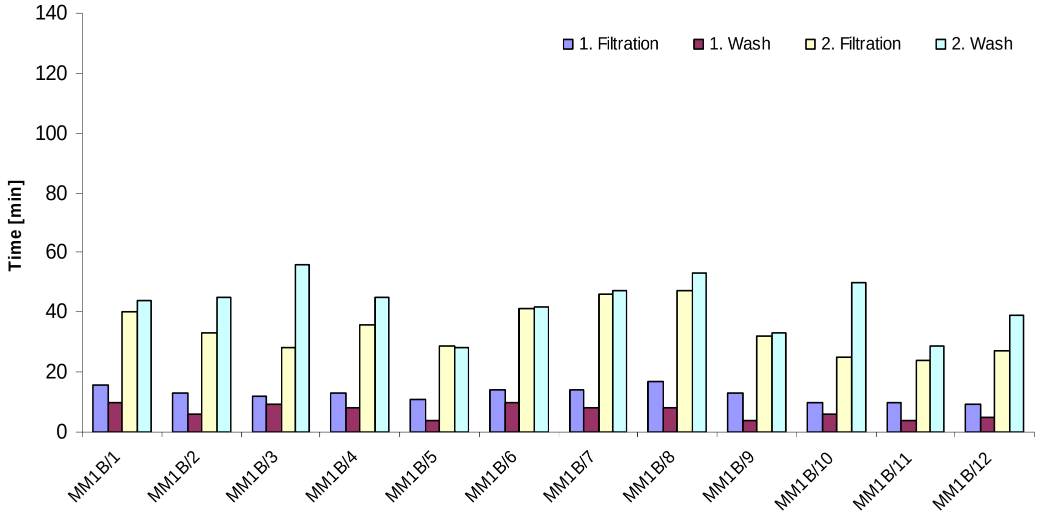


Figure 4 The filtration and washing times on the acidic precipitations series MM1A (pH 6) and MM1B (pH 8)

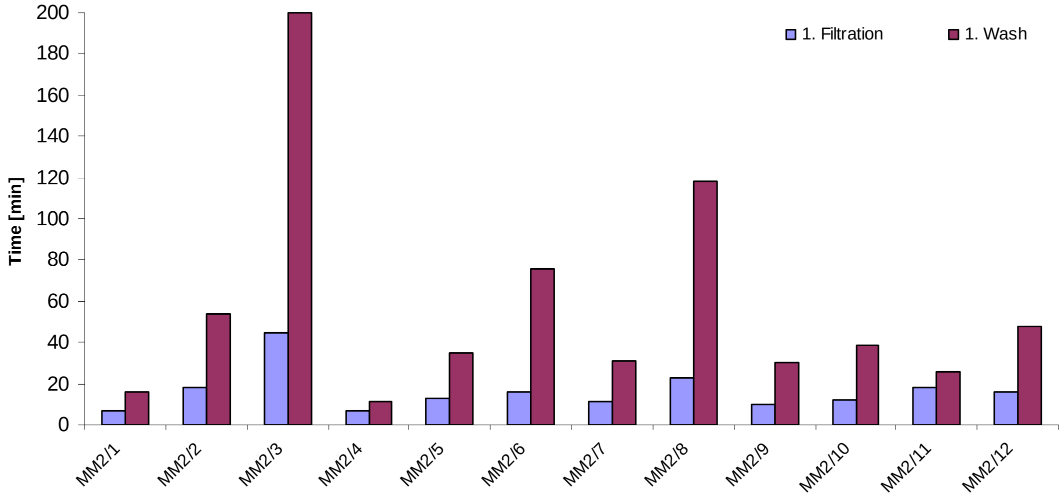


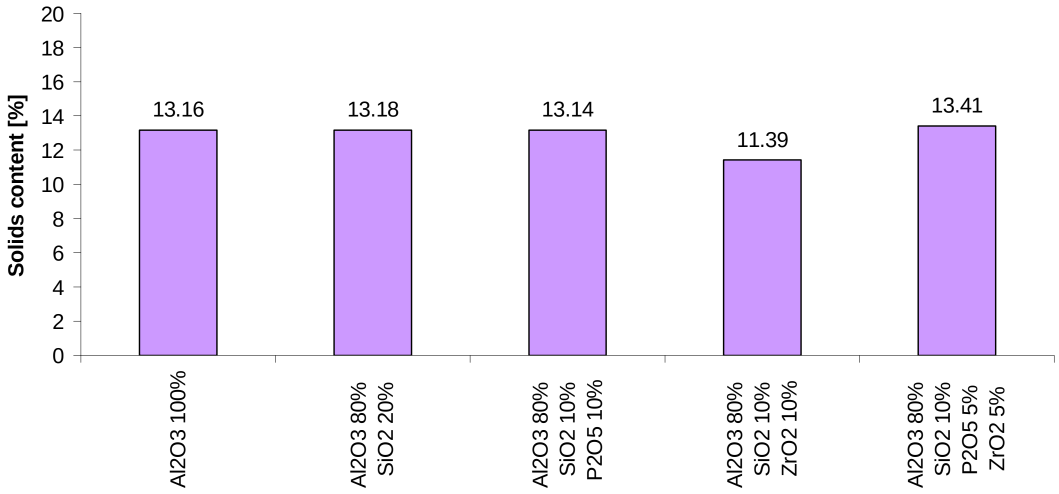
Figure 5 The filtration and washing times on the basic precipitations series MM2

11.1.4 Solids Content of Wet Cake

A pure alumina cake prepared by basic precipitation contains quite little water compared to a cake prepared by acidic precipitation (Appendix 3). In all cases the solids content decreased in the basic precipitations compared to pure alumina cake. The solids content seemed to be fairly steady in the acidic precipitations. Some of the surface treatment chemicals used seemed to have a negative effect on the solids content. The cakes that were precipitated from an acidic precursor to the final pH of 6 had solids content of 12 - 15 m-% and, in proportion to the final pH of 8, of 11 - 13 m-%. The precipitations from basic precursors caused solids content to vary widely, i.e. between 19 and 77 m-%.

The precipitations that contained titanium and silicon seemed to have an effect on the solids content. The presence of silicon in basic treatments decreased solids content, but in the acidic precipitations had an opposite effect (Figure 6). The presence of TiO_2 decreased the solids content in both treatment bases (Figure 7).

a)



b)

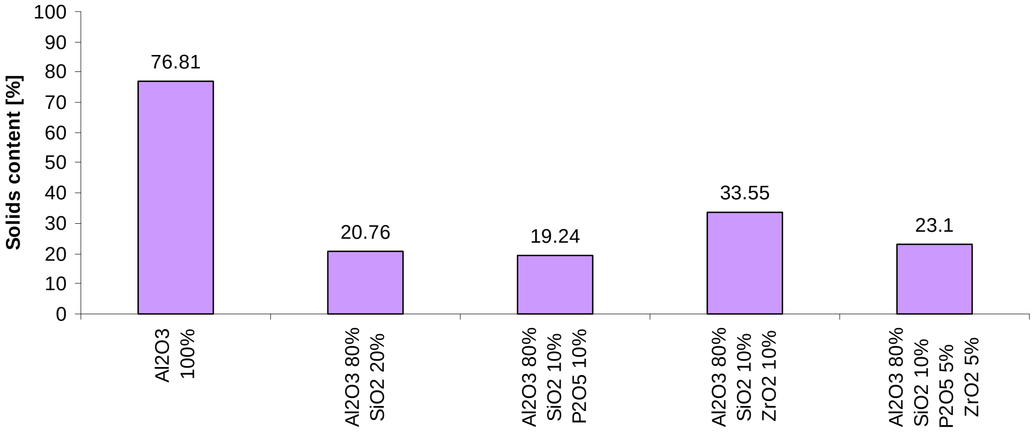


Figure 6 Solids content of the cake in a) the acidic precipitation end pH 8 (MM1B) and in b) the basic precipitation end pH 7 (MM2) the point of view SiO_2

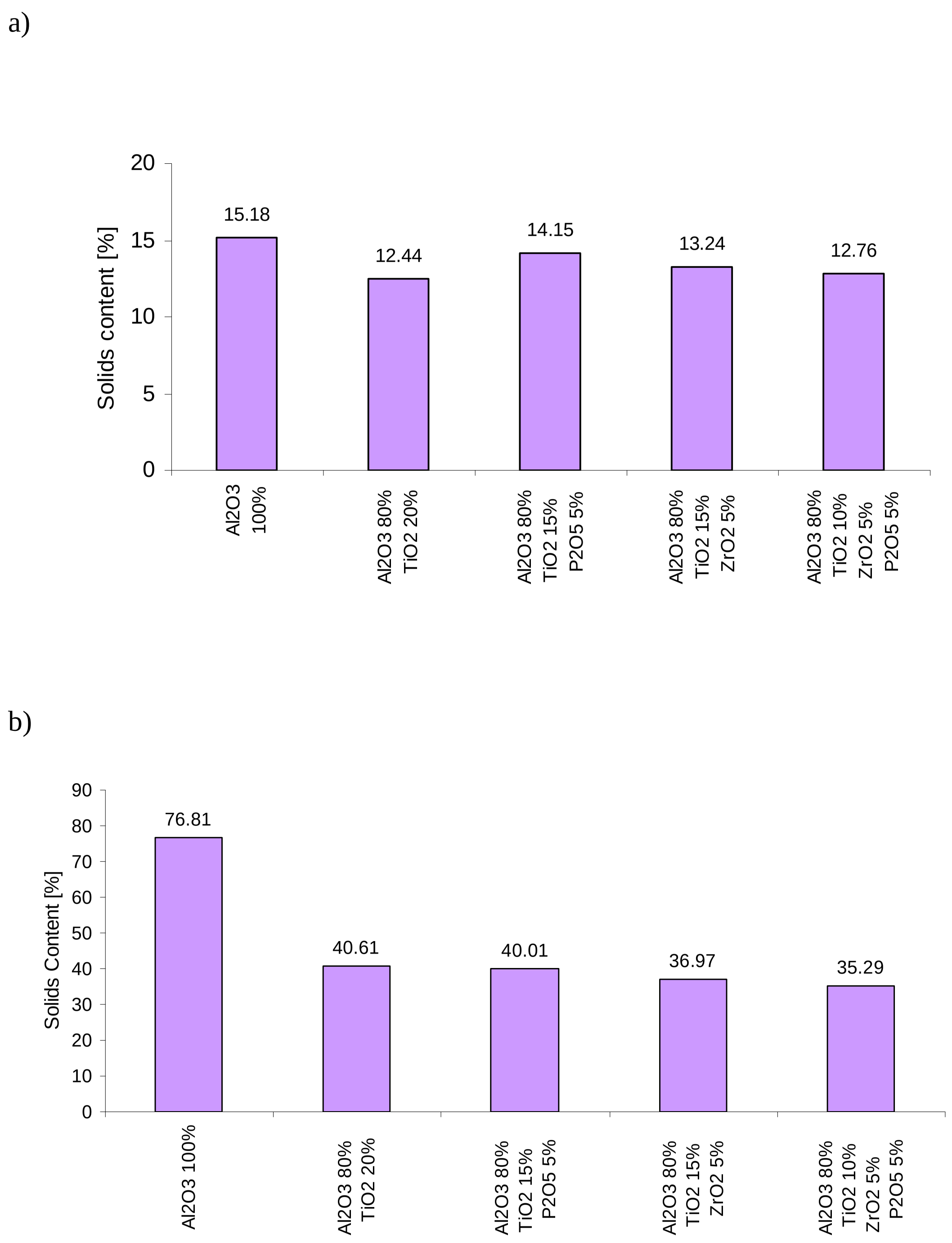


Figure 7 Solids content of the cake in a) the acidic precipitation end pH 6 (MM1A) and in b) the basic precipitation end pH 7 (MM2) the point of view TiO_2

11.2 Crystallinity of the Samples

One of the main interests of this study was in the crystallinity of the samples. The structural order of the samples varied from amorphous to some degree of crystallinity (Appendix 4). With a few exceptions, the twelve samples of the series had the same structural order. Amorphous samples were either purely amorphous or amorphous with some crystalline AlO(OH) or $Al(OH)_3$ elements, pseudoboehmite. The crystalline samples were either bayerite, β- $Al(OH)_3$, or boehmite, α- AlO(OH), or both. The structural order of samples also seemed to have an effect on the samples' other properties. For example, the porosity of the sample correlates with the structural order and the porosity has an effect on the filtration and washing times of the sample cakes.

11.2.1 Acidic Precipitations

All the acidic samples neutralised to a final pH of 6 (MM1A) were amorphous. These samples were also porous and their sodium content was lower than of the crystallite samples. The filtration and washing times of these cakes were longer than those of the cakes in the other series. Precipitation MM1A/12 was the only one which also contained crystalline AlO(OH) elements (Figure 8).

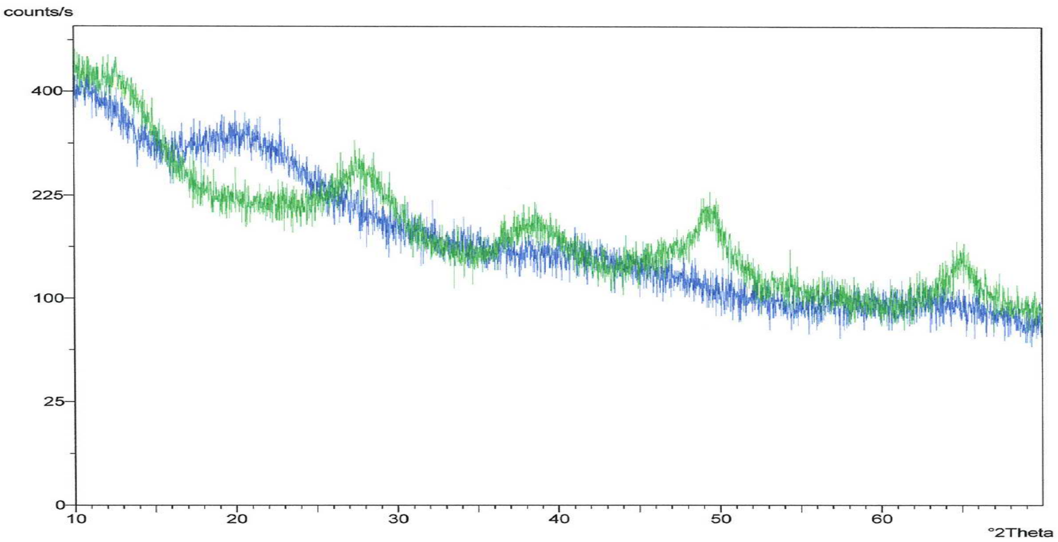


Figure 8 Two different amorphous samples: amorphous sample MM1A/1 (blue line) and amorphous sample MM1A/12 was pseudoboehmite, contained crystalline $Al(OH)_3$ elements (green line)

All the acidic samples neutralised to the end pH 8 (MM1B) seemed to be similar in structural form, pseudoboehmite. All those samples were amorphous, with crystalline boehmite, AlO(OH), elements. The porosity of these precipitates was smaller than that of the amorphous series samples. Filtration and washing of these cakes took place a little faster than series MM1A cakes. The sodium content of the samples was a little higher.

11.2.2 Basic Precipitations

With the exception of three samples that contained silicon dioxide, the basic samples neutralised to the final pH of 7 (MM2) had a crystalline structural order. The amorphous character of silicon dioxide dominated in the samples. The three samples MM2/5, MM2/10 and MM2/12 were amorphous and contained crystalline $Al(OH)_3$ and AlO(OH) elements (Figure 9). These pseudoboehmite samples were more porous than the other samples of the series MM2.

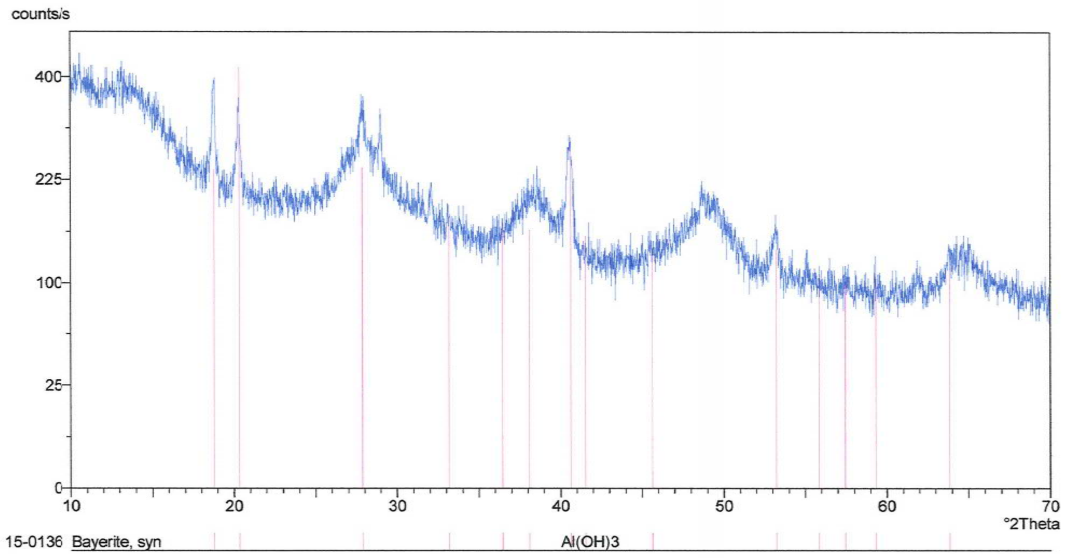


Figure 9 Amorphous sample by basic precipitation, MM2/12, included crystalline Al(OH)3 elements

The crystallite structural form of the samples was mostly bayerite but also boehmite existed. The spectrum of boehmite samples had a few more peaks than did the bayerite spectrum (Figures 10 and 11). One peaked at the value 14.5 and others are aligned on the bayerite peaks. These peaks are clearly in evidence in the samples MM2/1, 4 and 7. Samples MM2/2 and MM2/9 also show these peaks, but they are weaker. These samples have only one common factor: acidic surface treatment chemical. All these samples were prepared from the acidic surface treatment chemicals aluminium sulphate, titanyl sulphate or zirconium sulphate.

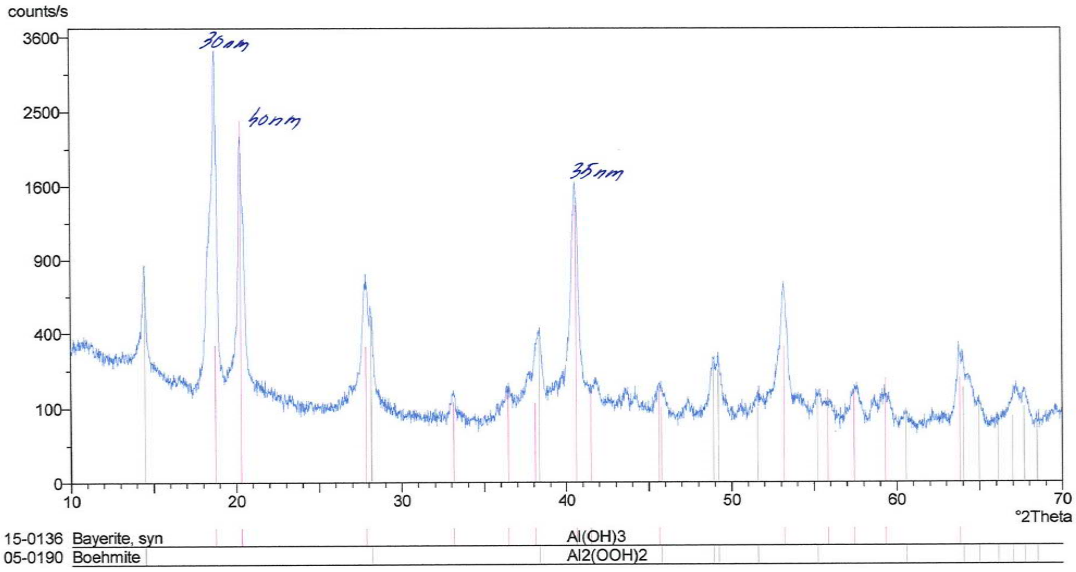


Figure 10 XRD spectrum and crystal size of sample MM2/1, prepared from a pure alumina sample by basic precipitation

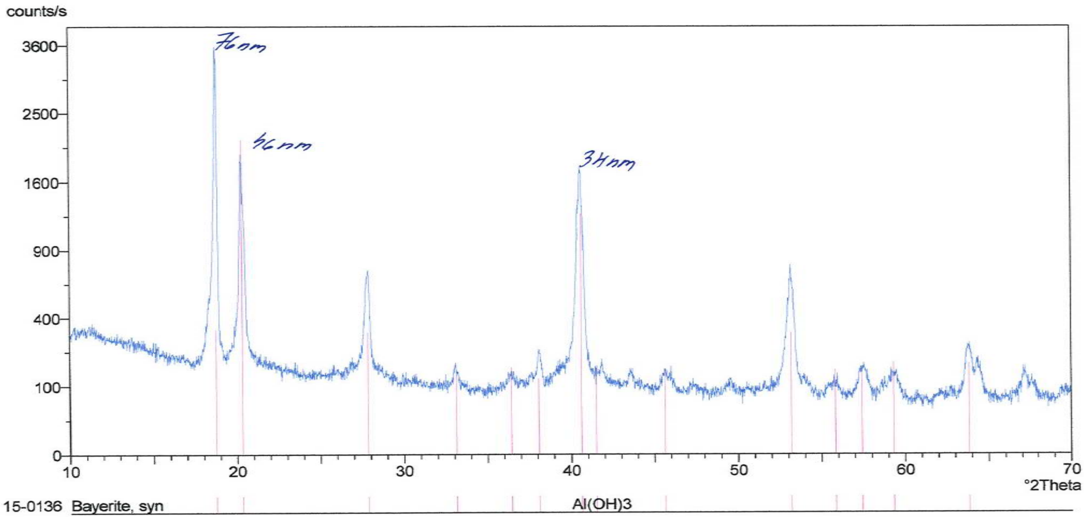


Figure 11 XRD spectrum and crystal size of sample MM2/3, prepared from alumina and phosphorous pent-dioxide by basic precipitation

11.2.3 Crystal Size of Crystallite Samples

The crystal size of the samples was calculated from the XRD-spectra (Figure 11). The average XRD-crystal size was calculated from the half-width of the peak. The first five samples of series MM2 were measured and the results are shown on Table 8.

Table 8 Crystal size of samples prepared by basic precipitation

	MM2/1	**MM2/2/1**	**MM2/2/2**	**MM2/3**	**MM2/4**	**MM2/5**
Crystal sizes observed [nm]	30/35/40	37/46/67	34/43/44	34/46/76	38/42/45	3/50/82/>100

The addition rate of the precipitate had an effect on the crystal size of the sample. Precipitation MM 2/2 was prepared twice (see Point 11.5) with two different addition rates of titanyl sulphate. The lower the addition rate of precipitate, the smaller the crystal size (Table 8).

11.3 Chemical Composition and Chemical Properties

The end product of the chemical oxide composition of the precipitations was dependent on the chemicals added. The end products contained the hydroxides added and also sodium and sulphur, the left-over precipitant and precursors, as soluble salts. Sodium and sulphur are left-over precipitants and precursors. Another of the main focuses of these studies was to minimise the sodium and sulphate contents in the end product. The chemical contents were analysed with XRF and the results were given in oxide form. Specific resistance gives information on the sodium content of the sample. The chemical content of the intermediate samples was also analysed and those results are represented in Point 11.3.4. Chemical properties such as moisture, residual mass and photoactivity of the samples were measured.

11.3.1 Sodium and Sulphate Contents

The sodium content of the samples was dependent on the filtration and washing times. In addition, the structural order of the samples had an effect on filtration and on the washing properties of the sample. The precipitation method and the end pH in turn had an effect on the sulphate content of the end products.

Table 9 Sodium (Na_2O) and sulphate (SO_3) contents (m-%) in three different precipitation series

MM1A	**/1**	**/2**	**/3**	**/4**	**/5**	**/6**	**/7**	**/8**	**/9**	**/10**	**/11**	**/12**
Sodium [m-%]	1,09	0,97	0,48	**1,11**	0,35	1,10	0,73	**0,15**	0,61	0,44	0,65	0,27
Sulphate [m-%]	**29,32**	22,98	**18,04**	22,42	21,13	22,14	21,08	18,79	19,16	18,36	21,84	20,45
MM1B	**/1**	**/2**	**/3**	**/4**	**/5**	**/6**	**/7**	**/8**	**/9**	**/10**	**/11**	**/12**
Sodium [m-%]	1,22	0,86	0,99	0,99	0,97	1,26	1,38	1,04	**0,37**	**1,41**	0,68	0,45
Sulphate [m-%]	**18,08**	9,22	**3,31**	10,05	8,39	9,39	9,03	6,06	5,88	3,96	8,37	5,74
MM2	**/1**	**/2**	**/3**	**/4**	**/5**	**/6**	**/7**	**/8**	**/9**	**/10**	**/11**	**/12**
Sodium [m-%]	1,32	2,74	3,91	**0,37**	4,41	3,87	1,74	5,46	3,53	3,81	2,30	**9,27**
Sulphate [m-%]	0,48	0,18	0,70	0,19	0,12	0,17	**0,09**	0,11	0,10	0,10	2,92	**8,04**

The acidic mixed precipitations contained less sodium and sulphate in comparison to the pure alumina sample. Those samples were amorphous-structured. The results of the acidic precipitated samples neutralised to an end pH of 8 varied more than samples neutralised to the end pH 6. The basic mixed samples contained more sodium than did the pure alumina samples. Sample MM2/12 contained a large amount of sodium and sulphates (Table 9).

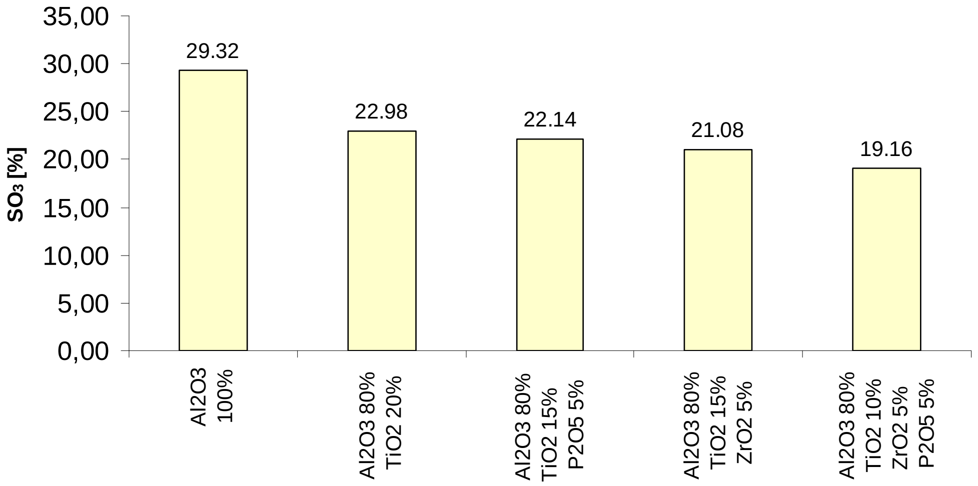


Figure 12 Sulphate content of acidic precipitation (pH 6) samples from the point of view of TiO_2

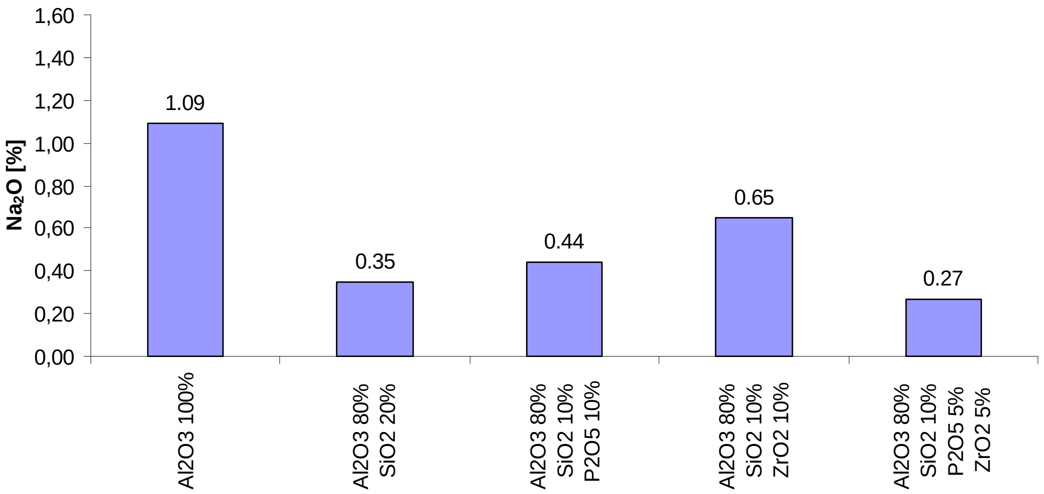


Figure 13 Sodium content of acidic precipitation (pH 6) samples from the point of view of SiO_2

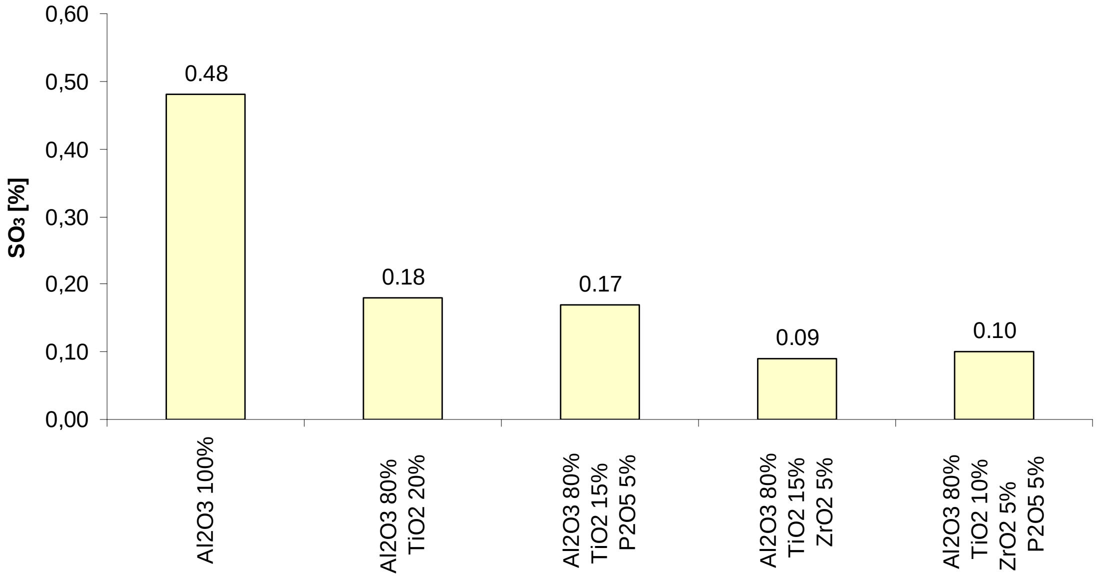


Figure 14 Sulphate content of basic precipitation (pH 7) samples from the point of view of TiO_2

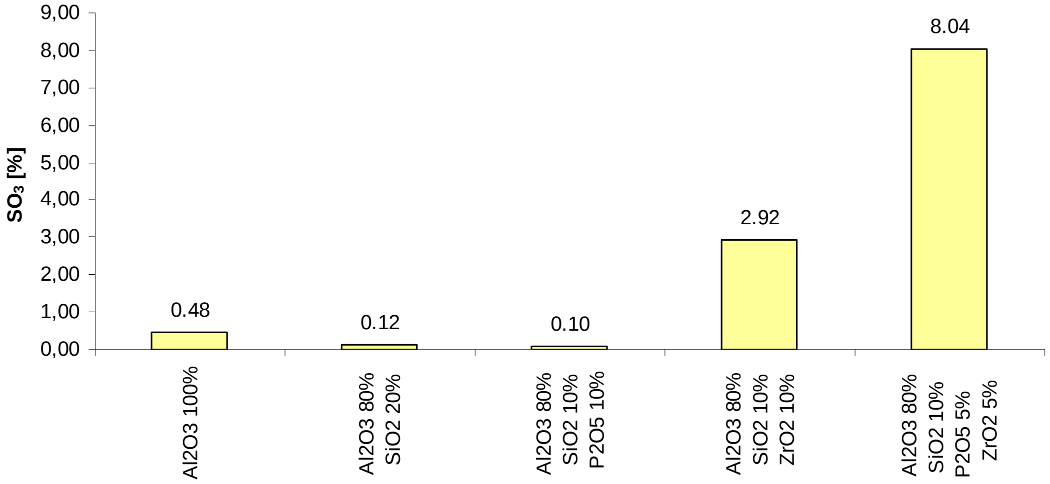


Figure 15 Sulphate content of basic precipitation (pH 7) samples from the point of view of SiO_2

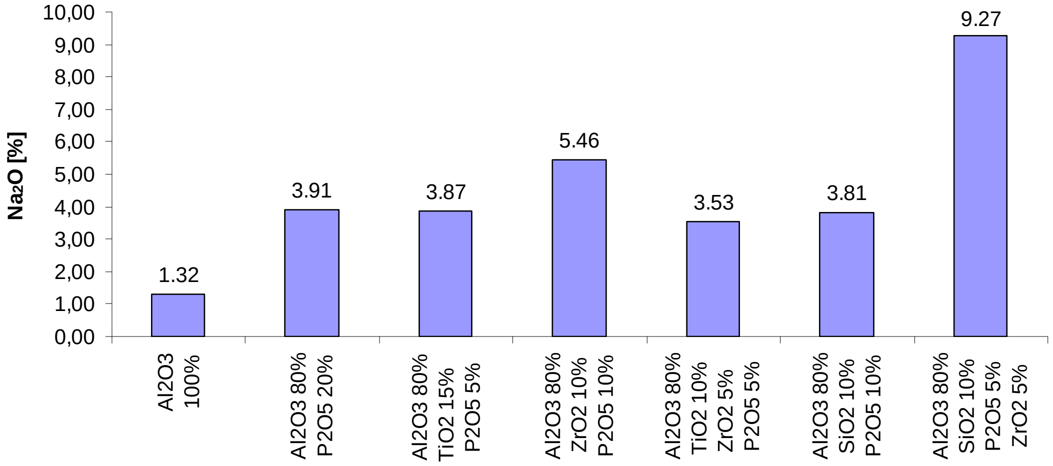


Figure 16 Sodium content of basic precipitation (pH 7) samples from the point of view of P_2O_5

11.3.2 Specific Resistance of the Samples

The specific resistance values of the samples were in relation with the sodium content of the samples. The lower the sodium contents of the sample, the higher the specific resistance. The specific resistance varied as widely as did the sodium content of the sample. The specific resistance values were highest in the acidic precipitated series MM1A (Figure 17) neutralised to an end pH 6 and lowest in basic precipitated series MM2.

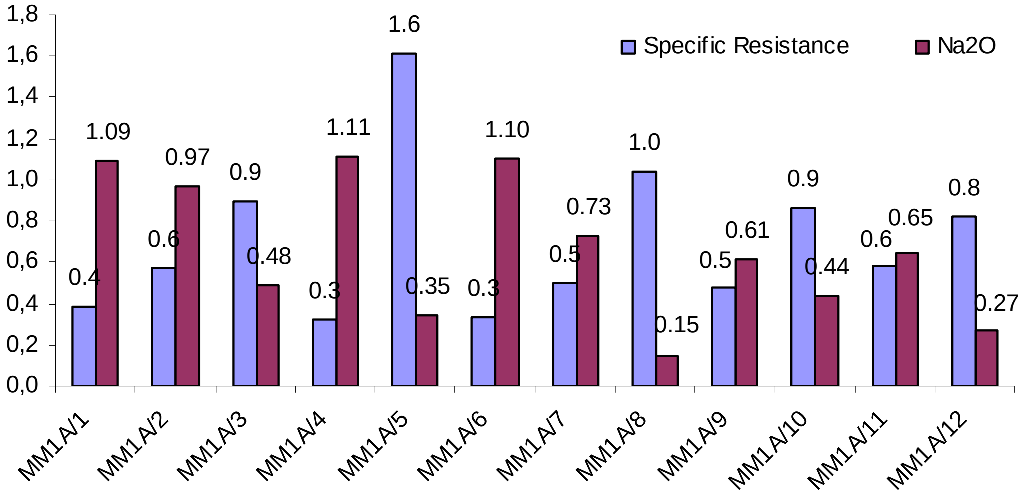


Figure 17 Specific resistance and Na_2O content of samples in series MM1A

11.3.3 Precipitated Hydroxide Contents

The addition of all of the surface treatment chemicals was calculated as oxides. All precipitations consisted mostly of alumina given as about 80 m-% Al_2O_3 and the rest of the solution was some another hydroxide with the exception of the first ones, which were pure alumina. The final hydroxide contents reached were varied (Appendix 1).

The final pH of the precipitation and the precipitation base - weather acidic or basic - greatly affected the chemical contents of the end product (Figure 18). The solutions precipitated from the basic base contained more alumina than did those from the acidic base (Table 10). The basic precipitations contained 65 – 98 % alumina. In acidic precipitations neutralised to an end pH of 6, the alumina content varied from 55 to 69 %, and from 61 to 80 % in those neutralised to an end pH of 8. Zirconium hydroxide causes lower alumina contents in acidic precipitations (Appendix 1).

Table 10 The average Al_2O_3 contents in on all three series

	MM1A (pH 6)	**MM1B (pH8)**	**MM2 (pH7)**
Average Al_2O_3 content [m-%]	62.47	71.23	75.43

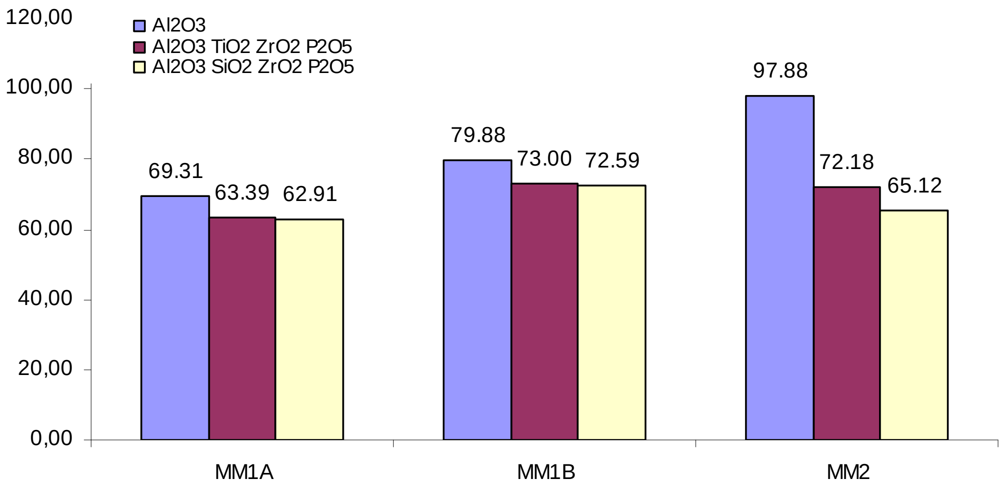


Figure 18 A comparison between three different precipitation methods: acidic pH 6 (MM1A), acidic pH 8 (MM1B) and basic pH 7 (MM2) and three compositions pure alumina, two mixed precipitations.

In addition, the added surface treatment chemicals' hydroxide content of the final products varied. In both, basic and acidic, precipitations zirconium hydroxide was precipitated most perfectly (Figure 19). In acidic precipitation to the final pH of 6 other precipitated hydroxides were precipitated approximately two percents less than the calculated addition estimated (Figure 20). In acidic precipitations to the final pH of 8 and in basic precipitations all other chemical hydroxides precipitated better (Figure 21).

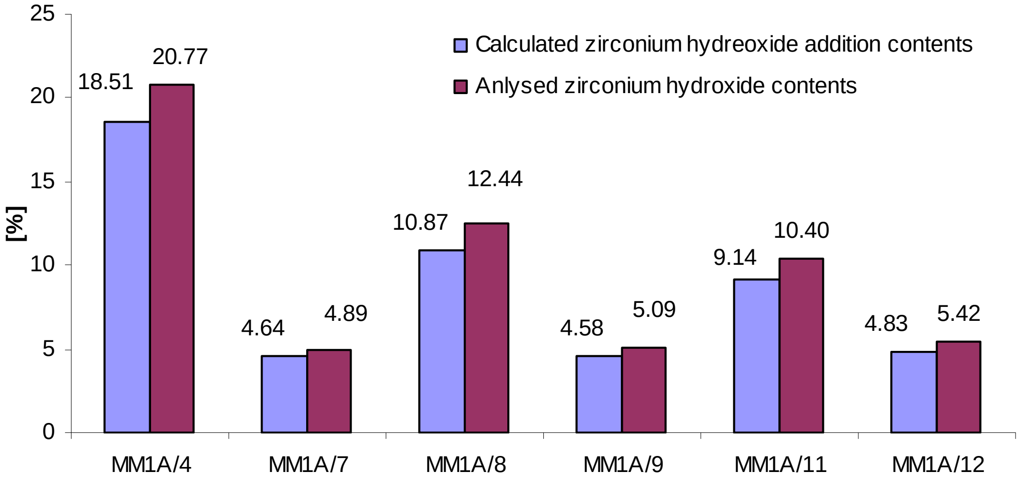


Figure 19 Precipitated zirconium hydroxides (in acidic precipitations) in comparison with added and analysed concentrations

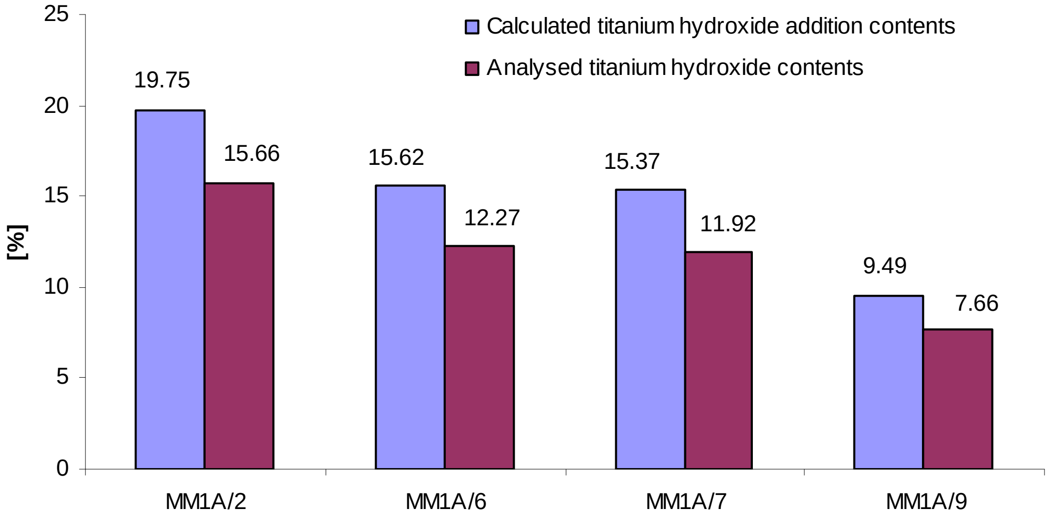


Figure 20 Precipitated titanium hydroxides (in acidic precipitations) in comparison with added and analysed concentrations (silicon and phosphorous acted similarly)

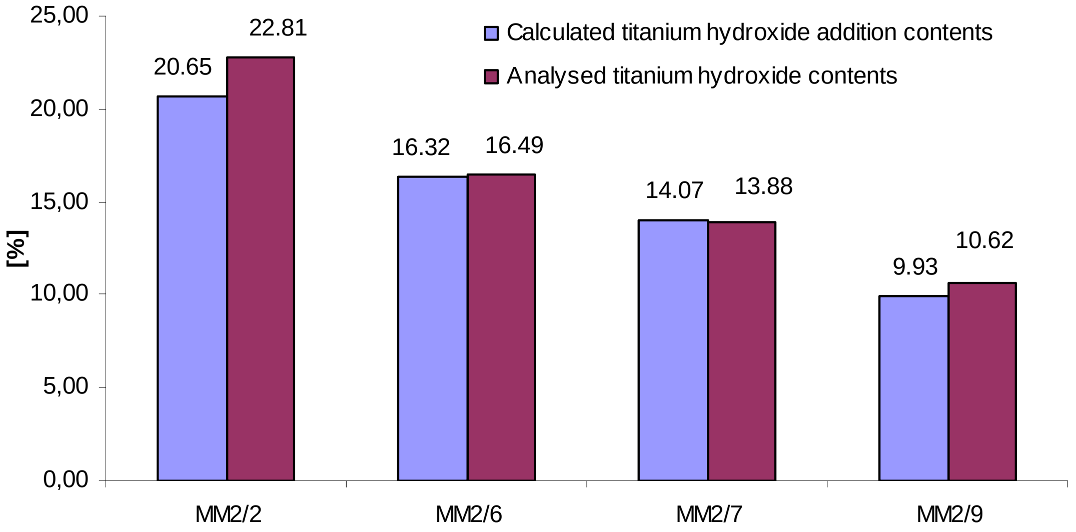


Figure 21 Precipitated titanium hydroxides (in basic precipitations) in comparison with added and analysed concentrations

11.3.4 Intermediate Samples

Intermediate samples were taken during the basic precipitations (Appendix 5). The intermediate samples were taken after all precipitate chemicals had been fed, and before the sulphuric acid feed was started. At this point of the precipitations, nearly half of total precipitated oxides of the end product had formed (Table 11). There were a few exceptions. Silicon was the only element which acted differently in each precipitation. Only a quarter of the silicon hydroxide seemed to be precipitated at that point.

Table 11 Percentage values of the intermediate samples of the oxide content compared with the precipitated oxides of the end product

	Al_2O_3 [%]	TiO_2 [%]	ZrO_2 [%]	SiO_2 [%]	P_2O_5 [%]
MM2/2/2 IS	66.02	46.73			
MM2/4 IS	48.06		29.52		
MM2/5 IS	31.47			22.36	
MM2/6 IS	64.22	52.70			25.53
MM2/7 IS	64.95	50.94	43.62		
MM2/8 IS	53.06		37.08		35.59
MM2/9 IS	59.67	58.87	54.02		26.71
MM2/10 IS	39.09			25.82	58.51
MM2/11 IS	36.98		58.08	23.91	
MM2/12 IS	55.97		71.30	36.31	75.19

11.3.5 Moisture Content and Loss On Ignition (TGA)

The moisture content and loss on ignition were measured from the first five samples in all of the series. The loss on ignition values increased when the moisture content decreased. The moisture level was a little lower in the acidic samples precipitated to a final pH of 6 than in those precipitated to an end pH of 8. The moisture content varied from 5.7 % to 7.7 % in precipitations with end pH of 6, and from 6.6 % to 8.7 % with end pH of 8, (Table 12). In basic precipitations, the moisture content varied from 0.3 % to 6.8 %. The moisture content values increased in both series produced by acidic precipitations, and also in basic precipitations, compared to pure alumina samples.

Table 12 Results of TGA measurements of moisture content and loss on ignition from Series a) MM1A/1-5, b) MM1B/1-5 and c) MM2/1-5

a)

	MM1A/1	**MM1A/2**	**MM1A/3**	**MM1A/4**	**MM1A/5**
Moisture [%]	5.67	6.45	7.71	6.43	6.61
LOI [%]	41.25	36.49	32.37	36.52	34.80

b)

	MM1B/1	**MM1B/2**	**MM1B/3**	**MM1B/4**	**MM1B/5**
Moisture [%]	6.61	8.23	8.68	7.73	7.41
LOI [%]	30.94	24.40	19.62	24.61	23.59

c)

	MM2/1	**MM2/2**	**MM2/3**	**MM2/4**	**MM2/5**
Moisture [%]	0,34	1.85	2.40	1.92	6.77
LOI [%]	32.48	29.16	29.65	29.30	17.92

11.4 Physical Properties

Some physical properties of the samples were measured by focusing on surface properties. The colour measurements were made to reveal possible differences in the brightness and tone values among the samples. Specific surface and pore volumes of the sample as well as oil absorption give information on the porosity of the samples. Photoactivity/stability measurements give information on the weather-resistance of the sample. The wear resistance of the samples was measured with a four-hour period of wet grinding of the samples.

11.4.1 Brightness

A surface-treated pigment should be as white as possible. For a totally white powder reflecting all visible light, the optimal brightness value is 100. The optimal tone value is zero, meaning that the measured powder is neither yellowish nor bluish. The brightness of the mixed precipitated samples was compared with that of the pure alumina samples. The brightness value of the pure alumina powders produced through acidic precipitations was higher - almost 99 - compared to that of the basic ones, which was approx. 98. In acidic precipitations, a higher end-pH seemed to have a negative effect on brightness.

The combinations by basic precipitations increased the brightness value, whereas the combinations by acidic precipitations diminished it (Appendix 6). Both cases presented one exception. The presence of phosphorous increased the brightness value to almost 99 in acidic precipitations with an end pH of 8. In basic precipitations the presence of phosphorous and zirconium decreased the brightness value.

Two of the surface treatment chemicals acted with more intensity than the other chemicals. Silicon seemed to have the most positive effect on the brightness and titanium the most negative effect (Figure 22).

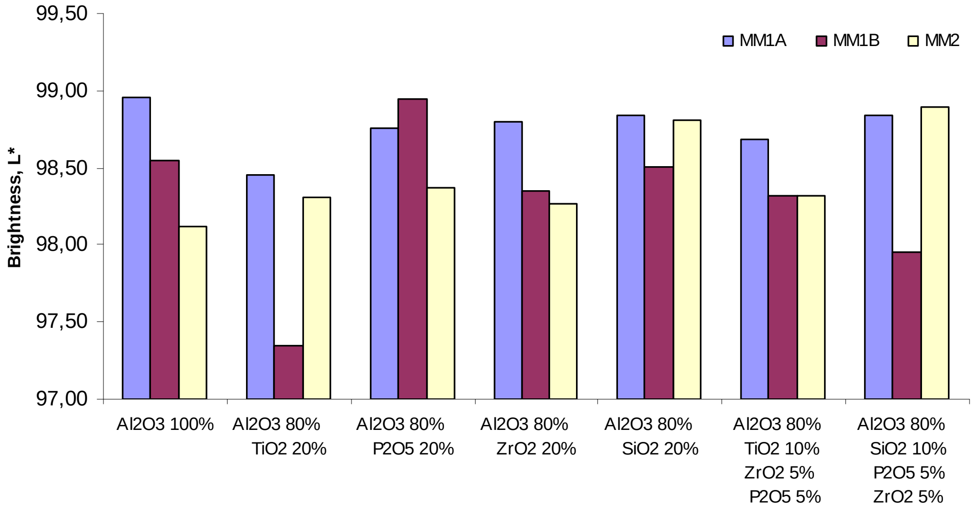


Figure 22 The brightness of the samples

11.4.2 Oil Absorption, Specific Surface and Pore Volumes of the Samples

Oil absorption recreates the porosity of the sample. It correlates with specific surface and pore volumes of the sample as well as with structural order.

The amorphous sample was more porous than the crystalline sample (Appendix 7). The oil absorption value of the amorphous sample was between 70 - 195 %, whereas that of the crystalline sample was between 35 - 100 %. The same is also seen in the values of specific surface area and pore volume of the samples (Figure 23). The values of specific surface of the amorphous samples with some crystalline $Al(OH)_3$ elements, were a little higher than those of pure amorphous samples.

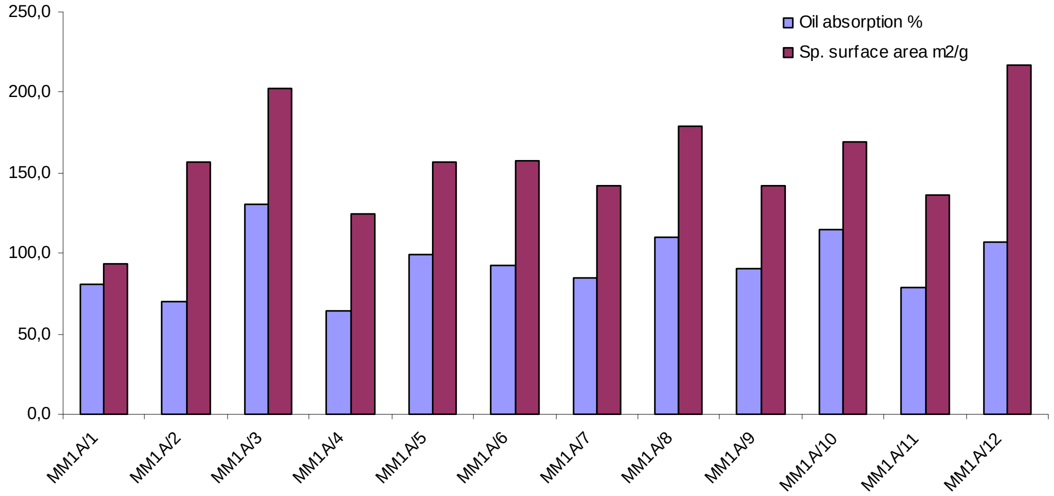


Figure 23 Oil absorption and specific surface area values of acidic precipitated samples

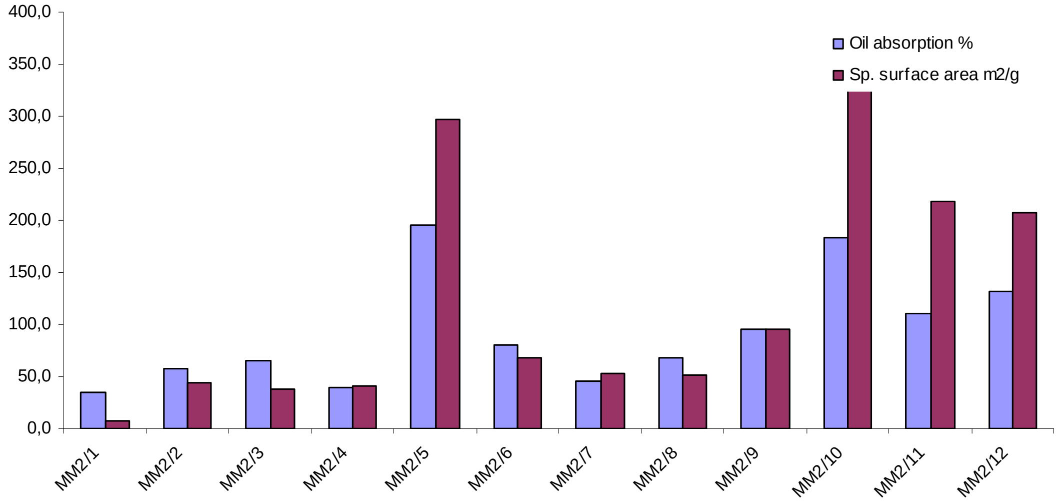


Figure 24 Oil absorption and specific surface area values of basic precipitated samples

Most porous samples of the basic precipitations contained silicon hydroxide (Figure 24). In sample MM2/5, where aluminium (80 % as Al_2O_3) was precipitated together with silicon (20% as SiO_2), the specific surface value was 297 m^2/g and the pore volume was 511 $*10^{-3}$ ml/g. The oil absorption value was 195 % in the sample. The sample was very light and acted most differently in all analyses.

The other porous sample was the acidic precipitated sample containing phosphorous. The presence of phosphorous increased the consumption of linseed oil and the specific surface area value (Figure 23). In mixed precipitations without silicon hydroxide, the porosity of phosphorous containing samples was not obvious. Porosity was high in precipitations where both phosphorous and silicon were present.

11.4.3 Particle Size

The particle size of the samples was measured with Malvern Mastersizer 2000 at those intervals during a four-hour period of wet grinding on rotating roller: after 30 minutes, 2 hours and 4 hours. The first five samples of all series were measured (Appendix 8). Four hours of wet grinding had a similar effect on particle size reduction as a function of time in precipitation series MM1A and MM2 samples (Figure 26). In both series particle size becomes smaller - on average 45 µm - after four hours' wet grinding.

In a comparison with pure alumina samples, the series acted differently. The particle size after four hours of grinding did not differ in the mixed samples of series MM1A compared with the pure alumina sample. All the samples' particle sizes were between 15 and 18 µm after four hours. Compared with alumina, the content of silicon and phosphorus of the basic precipitated sample had the greatest effect on the particle size (Figure 25). Also, the presence of silicon the particle size diminished and the presence of phosphorus the particle size increased when compared with pure alumina. In these samples the particle size varied from 13 to 34 µm after four hours' grinding.

The acid-precipitated samples of series MM1B were very hard. The particle size results from these samples were extraordinary. For example, the particle size of TiO_2 containing sample MM1B/2 increased after four hours' wet grinding. Only the sample prepared with pure alumina acted in a similar way as the other samples measured.

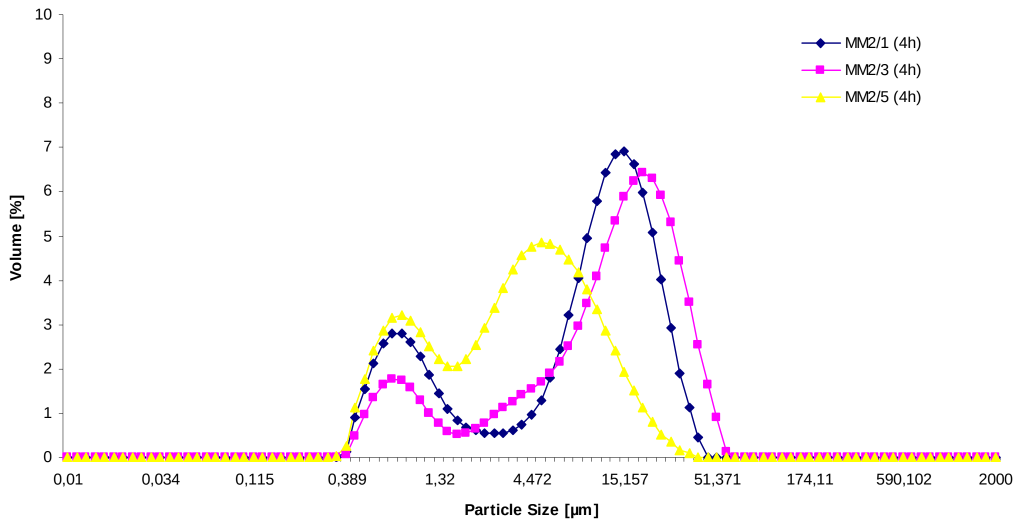


Figure 25 Particle size after four hours' wet grinding in basic precipitated samples MM2/1, MM2/3 and MM2/5

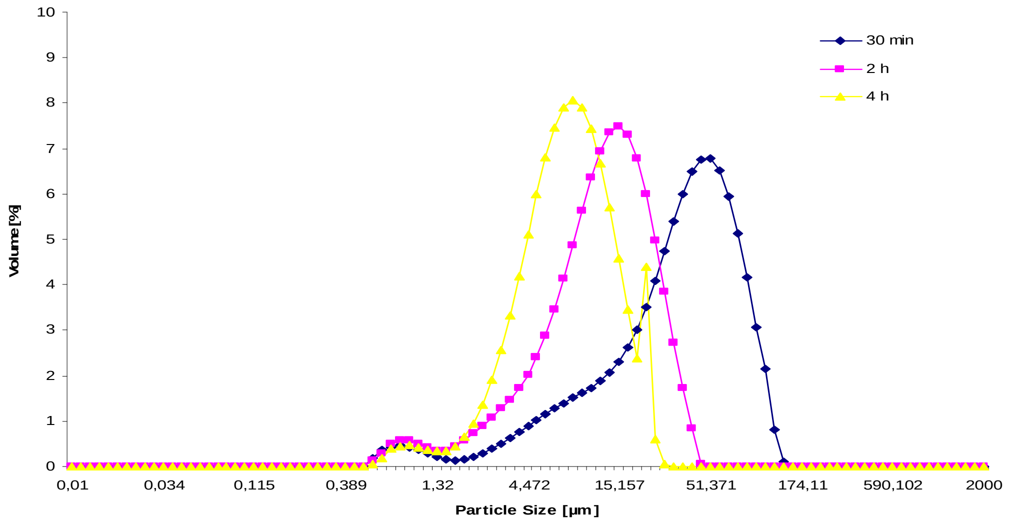


Figure 26 The effect of wet grinding on particle size in sample MM1A/4 (other samples in series MM1A and MM2 produced a similar figure)

11.4.4 Photostability

The inorganic coating chemicals on the surface of a pigment improve the weather-resistant of the pigment. Absorption of UV radiation by TiO_2 can lead to the generation of hydroxyl radicals, which causes the pigment to act as a photocatalyst. To ensure that the actual effect is beneficial, the photocatalytic effect of the pigment is minimised by coating the pigment with hydrous oxides, e.g., silica and alumina, during manufacture. In this study the measured samples proved inorganic surface treatments to be photostable. All samples had superior or excellent photostability. Only the basic sample containing aluminium (80 % Al_2O_3) and titanium (20 % TiO_2) showed an increase in photostability (Table 13).

Table 13 Photostability of samples measured

	MM2/1	**MM2/2**	**MM2/3**	**MM2/4**	**MM2/5**	**MM2/9**	**MM2/12**
Acetone Formation Rate [ppm/h]	1	9	1	1	2	1	4
	MM1A/2	**MM1A/9**	**MM1A/12**	**MM1B/2**	**MM1B/9**	**MM1B/12**	
Acetone Formation Rate [ppm/h]	0	0	4	2	1	0	

11.4.5 Isoelectric Point

Zeta potential has significance in several surface chemical phenomena. Zeta potential causes individual particles either to repel each other, resulting in dispersion stability, or to attract each other, resulting in flocculation. During the production of TiO_2 pigments, flocculation and dispersing play important roles. The pigment should be well dispersed in water during wet milling. Flocculation is needed when the TiO_2 pigment is filtered and washed. The particles flocculate at a pH close to the isoelectric point./14/ Dispersibility of TiO2 pigment should be excellent in various applications.

The surface charge measurement of the precipitated surface treatment hydroxides proved to be difficult. Six measurements were performed on samples MM2/1-5 and

MM2/12 from series MM2 (Appendix 7). These samples were soft and could be measured fairly easily (Figure 27). The measured samples MM1A/1-5 of the acidic precipitated series acted extraordinary (Appendix 9). Series MM1B were not measured because of the hardness of the samples. In the future it might be better to perform the measurement of the streaming current from wet samples whose dry content is known.

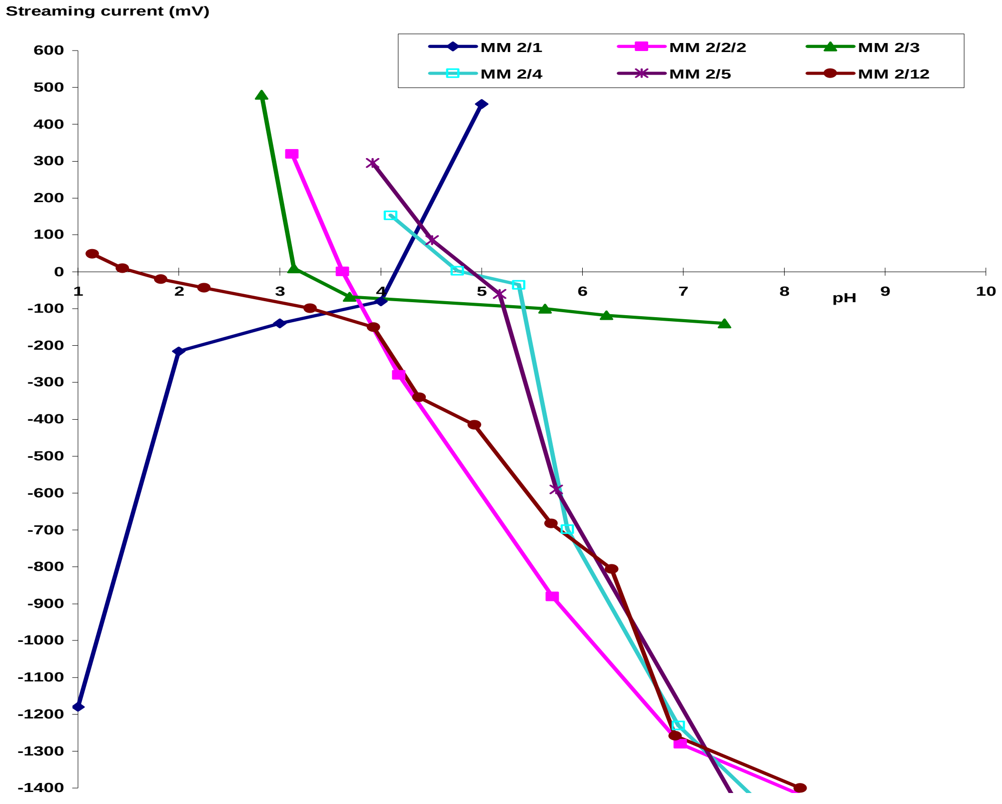


Figure 27 Measurements of streaming current from series MM2 as a function of pH

The isoelectric point of the samples measured varied in the basic precipitated samples. The results of the acidic samples were similar, with the exception of that of sample MM1A/5. The results are shown in Table 14.

Table 14 Measured isoelectronic points of samples

	/1	/2	/3	/4	/5	/12
MM2	4.2	3.6	3.2	4.8	4.9	1.5
MM1A	4.3	4.5	4.0	4.2	1.6	

11.5 Effect of Addition Rate of the Treatment Chemical

The first mixed basic precipitation was a revelation. Titanyl sulphate was added with sodium aluminate in the same way as in the acidic precipitations. In a basic base, this produced immediate flocculation. The precipitates used were subsequently added slowly, at a rate of 40 ml/min by a feeding pump, on sodium aluminate. The first precipitation MM2/2 was coded MM2/2/1 (quick addition rate) and the re-precipitated sample MM2/2/2 (slow addition rate). The analyse results of these samples differ from each other.

The first MM2/2/1 prepared was slightly more amorphous than MM2/2/2. The crystal size of MM2/2/2 was smaller than that of MM2/2/1 (see Point 11.2.3). This was also observed in the porosity of the samples. The value of the specific surface area and pore volume of the sample MM2/2/2 was fifth of sample MM2/2/1. The chemical content of the end products did not differ greatly. Only the sulphate content was higher on sample MM2/2/1. The intermediate samples differed more greatly (Table 15).

Table 15 Intermediate samples of two different precipitated samples MM2/2

	Al_2O_3	TiO_2	SO_3	Na_2O
MM2/2/1(IS)	30.39	7.68	28.61	33.15
MM2/2/2 (IS)	48.91	10.66	16.93	23.33

11.6 Reference Precipitation

The reference sample MM0B was prepared in order to link these studies to Tuomo Keskisaari's experiments. In this study, all the precipitation conditions were chosen according Keskisaari's studies. The precipitants were diluted in order to achieve totally amorphous alumina samples. The XRD-spectrum of reference sample is seen in Figure 28.

The reference precipitation was based on aluminium sulphate solution consisting of 100 % aluminium hydroxide given as Al_2O_3. As the precipitant 300 g NaOH/l was used. The final pH of the precipitation was pH 8. The results of the reference precipitation are documented in Appendix 10. These results were similar with the results of Tuomo Keskisaari's studies.

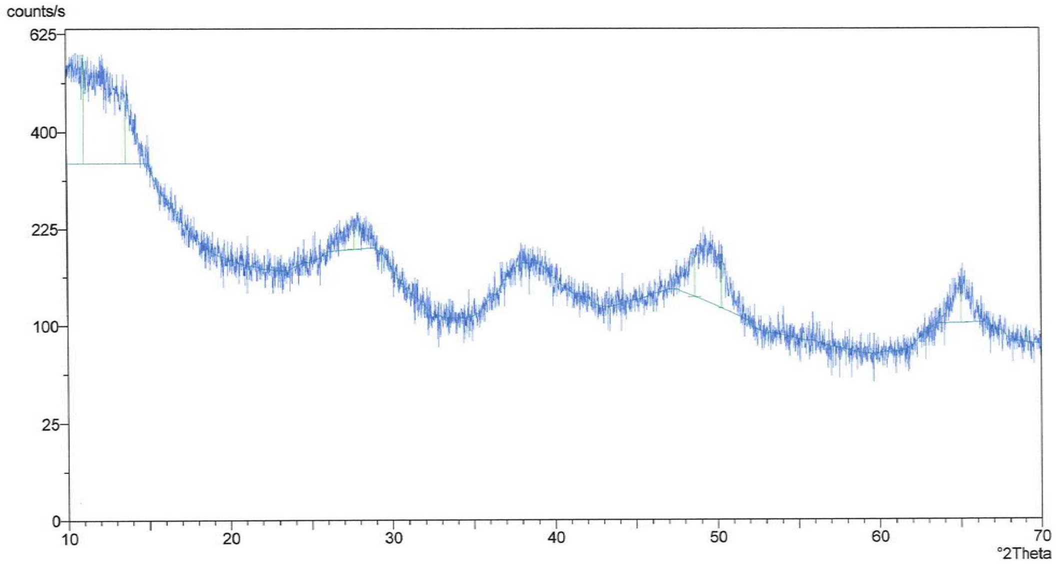


Figure 28 XRD spectrum of reference sample, prepared from pure alumina by acidic precipitation to a final pH of 8: amorphous with some crystalline AlO(OH) elements

12 RESULT CONSIDERATIONS

The goal of this bachelor’s thesis was to examine the effects of various surface treatment chemicals on the properties of aluminium hydroxide. The precipitation parameters were constant and were chosen according to Tuomo Keskisaari’s thesis. Only the surface treatment chemicals varied. The analyses focused on the degree of crystallinity, and on the chemical composition of the samples e.g. their sulphate (SO_3) and sodium (Na_2O) contents. In addition, specific surface area and pore size analyses as well as determination of oil absorption gave interesting results.

All samples with a similar structural form (boehmite and bayerite) seemed to act in a similar way. The surface treatment chemicals added had an effect on the structural form of the end product. The structural form of the sample had an effect on the sample’s chemical composition and physical properties. The water glass, which contained SiO_2, had the strongest effect on structural form. All acidic-based samples were amorphous and all alkali-based samples were crystalline. The amorphous samples were pseudoboehmite phase, either pure amorphous or amorphous with some crystalline elements. In basic precipitated amorphous silicon containing samples contained crystalline $Al(OH)_3$ or both $Al(OH)_3$ and $AlO(OH)$ elements. Crystalline samples were bayerite, β- $Al(OH)_3$, or boehmite, α- $AlO(OH)$, or both (Appendix 4).

The pure amorphous samples which were neutralised to a final pH of 6, were the most porous. These samples had long washing and filtration times, and also a low sodium- and a high sulphate content. Oil absorption values as well as the pore volumes of the samples were higher in comparison to the other samples. The specific surface of the samples was a little lower than that of amorphous samples with some crystalline $AlO(OH)$ elements.

The amorphous samples with some crystalline $AlO(OH)$ elements included all samples neutralised to a final pH of 8. In addition, one sample neutralised to a final pH of 6, and three samples, neutralised by alkali base to a final pH of 7, were amorphous with some crystalline elements. All these pseudoboehmite samples filtrated and washed faster than the amorphous ones. The porosity of the samples was lower than the samples of the series precipitated to a final pH of 6, but the specific surface was little higher.

The basic precipitation samples (series MM2) had a crystalline structure, with the exception of three samples which contained silicon dioxide. These crystalline samples washed and filtrated faster than the other samples. The sulphate content of the samples was lower, and the sodium content was higher than those of acidic based samples. These samples had lower porosity.

In many analyses the effect of the samples' structural order could also be observed. For example, the moisture content of the amorphous samples was higher than the crystalline-ordered samples. The amorphous samples acted extraordinary in surface charge analyses. These amorphous samples were much harder than the crystalline ones. In addition, it was difficult to perform the particle size measurements after four hours' wet grinding due to the hardness of the amorphous samples.

The precipitation conditions, acidic or basic, and the final neutralisation pH had a greater effect on the sodium and sulphate contents of the end product than did the crystallinity of the samples. In comparison to the pure alumina sample, in all cases, the surface treatment chemical added had an effect on the sodium and sulphate contents of the end product. All samples prepared with acidic precipitation had both a lower sulphate content and also a lower sodium content in comparison to the pure alumina sample, with the exception of one sample. In the basic mixed precipitated samples the sulphate content decreased, with the exception of two samples and sodium content increased in comparison to the pure alumina. In addition, in all cases of mixed precipitation, the porosity values - oil absorption, specific surface and pore volume of the samples - increased.

The brightness of the samples differed between the acidic and basic precipitated samples. In basic precipitations the surface treatment chemicals added increased the value of the brightness. The silicon had the most positive effect on brightness. In acidic precipitations, the surface treatment chemicals added had a negative effect on the brightness value of the samples. Titanyl sulphate addition in precipitations neutralised to a final pH of 6, had the most negative effect on the brightness.

13 CONCLUSIONS

All analyses proved that samples with a similar structural form seemed to act in a similar way. The influence of the structural form was seen for example in filtration and washing times, solids content of wet samples, values of porosity and the moisture level of dried samples. In addition, the processability of various samples with different forms was observed, e.g. the hardness of the amorphous samples, which prevented conductively some analyses. The structural order and precipitation conditions, the end pH and precipitation base seemed to affect the sodium and sulphate content in the samples. All surface-treatment chemicals added had a certain effect on the chemical or physical properties of the precipitated samples.

Silica had the most well-defined effect. The presence of silicon in basic treatments created amorphous samples. These samples were the most porous of the all basic precipitations. Amorphous silicon seemed to have the most positive effect on brightness. The presence of silicon in basic treatments decreased the solids content, but in acidic precipitations had an opposite effect. Compared with the pure basic treated alumina, the presence of silicon diminished the particle size after four hours of wet grinding. In the surface charge measurements, silica dominated more than the other surface treatment compounds.

Phosphorus had an effect on brightness, porosity and particle size. The presence of phosphorus increased the brightness value to almost 99 in acidic precipitations with an end pH of 8. In the basic precipitation, the presence of phosphorus decreased the brightness value. In the acidic precipitation, the phosphorus containing samples were porous. The presence of phosphorus hydroxide increased the consumption of linseed oil and the specific surface area value. In comparison with the pure basic treated alumina, the presence of phosphorus increased the particle size after four hours wet grinding.

Titanium had an effect on a few of the analysis results. All basic precipitated samples containing titanium formed crystalline bayerite and boehmite structures. The presence of titanium decreased the solids content in both the acidic and the basic treatment bases. Titanium containing samples were clearly hard and yellow. Titanium had the most negative effect on the brightness and tone values. The hardness of the samples containing titanium caused extraordinary results in some analyses. For example, due to the hardness of the acidic-treated samples containing titanium, the particle size grew after four hours of wet grinding. The basic sample prepared by aluminium sulphate and titanyl sulphate showed a decrease in the photostability value.

The presence of zirconium had the least effect on the treated samples. All the basic-treated samples containing zirconium formed crystalline bayerite and boehmite. In addition, the basic precipitates containing zirconium had the most positive effect on solids content. Zirconium hydroxide decreased the brightness value. These analyses are correlating to the crystalline structure of the sample.

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Precipitation Series Composition

Precipitation	Surface compound	Target concentration [%]	Calculated concentration* [%]	Analysed final concentration [%]
MM1A/1	Al_2O_3	100	100	69.31
MM1A/2	Al_2O_3	80	80.25	60.29
	TiO_2	20	19.75	15.66
MM1A/3	Al_2O_3	80	80.66	66.13
	P_2O_5	20	19.34	15.11
MM1A/4	Al_2O_3	80	80.49	54.95
	ZrO_2	20	18.51	20.77
MM1A/5	Al_2O_3	80	80.14	63.12
	SiO_2	20	19.86	15.23
MM1A/6	Al_2O_3	80	79.32	60.91
	TiO_2	15	15.62	12.27
	P_2O_3	5	5.06	3.46
MM1A/7	Al_2O_3	80	80.00	61.15
	TiO_2	15	15.37	11.92
	ZrO_2	5	4.64	4.89
MM1A/8	Al_2O_3	80	78.62	60.76
	P_2O_5	10	10.51	7.41
	ZrO_2	10	10.87	12.44
MM1A/9	Al_2O_3	80	81.00	63.39
	TiO_2	10	9.49	7.66
	ZrO_2	5	4.58	5.09
	P_2O_5	5	4.93	3.46
MM1A/10	Al_2O_3	80	79.39	65.96
	P_2O_5	10	10.14	7.69
	SiO_2	10	10.46	7.43
MM1A/11	Al_2O_3	80	80.73	60.71
	ZrO_2	10	9.14	10.40
	SiO_2	10	10.13	6.11
MM1A/12	Al_2O_3	80	79.26	62.91
	SiO_2	10	10.71	7.02
	ZrO_2	5	4.83	5.42
	P_2O_5	5	5.19	3.65

*Based on analyses :

Aluminium sulphate	Al_2O_3	77.4 g/l
Titanyl sulphate	TiO_2	76.2 g/l
Zirconium sulphate	ZrO_2	184.0 g/l
Calgon	P_2O_5	98.9 g/l
Water glass	SiO_2	68.0 g/l

Precipitation Series Composition

Precipitation	Surface compound	Target concentration [%]	Calculated concentration* [%]	Analysed final concentration [%]
MM1B/1	Al_2O_3	100	100.00	79.88
MM1B/2	Al_2O_3	80	80.25	69.93
	TiO_2	20	19.75	19.52
MM1B/3	Al_2O_3	80	80.66	77.05
	P_2O_5	20	19.34	18.19
MM1B/4	Al_2O_3	80	80.49	60.77
	ZrO_2	20	18.51	27.27
MM1B/5	Al_2O_3	80	80.14	72.66
	SiO_2	20	19.86	17.70
MM1B/6	Al_2O_3	80	79.32	69.12
	TiO_2	15	15.62	15.86
	P_2O_3	5	5.06	4.11
MM1B/7	Al_2O_3	80	80.00	67.08
	TiO_2	15	15.37	15.39
	ZrO_2	5	4.64	6.78
MM1B/8	Al_2O_3	80	78.62	68.16
	P_2O_5	10	10.51	8.10
	ZrO_2	10	10.87	16.11
MM1B/9	Al_2O_3	80	81.00	73.00
	TiO_2	10	9.49	9.86
	ZrO_2	5	4.58	6.69
	P_2O_5	5	4.93	4.00
MM1B/10	Al_2O_3	80	79.39	74.82
	P_2O_5	10	10.14	9.57
	SiO_2	10	10.46	10.05
MM1B/11	Al_2O_3	80	80.73	69.70
	ZrO_2	10	9.14	13.46
	SiO_2	10	10.13	7.36
MM1B/12	Al_2O_3	80	79.26	72.59
	SiO_2	10	10.71	8.98
	ZrO_2	5	4.83	7.41
	P_2O_5	5	5.19	4.48

* Based on analyses :

Aluminium sulphate	Al_2O_3	77.4 g/l
Titanyl sulphate	TiO_2	76.2 g/l
Zirconium sulphate	ZrO_2	184.0 g/l
Calgon	P_2O_5	98.9 g/l
Water glass	SiO_2	68.0 g/l

Precipitation Series Composition

Precipitation	**Surface compound**	**Target concentration [%]**	**Calculated concentration* [%]**	**Analysed final concentration [%]**
MM2/1	Al_2O_3	100	100.00	97.88
MM2/2	Al_2O_3	80	79.35	74.08
	TiO_2	20	20.65	22.81
MM2/3	Al_2O_3	80	80.75	76.90
	P_2O_5	20	19.25	18.31
MM2/4	Al_2O_3	80	80.09	72.82
	ZrO_2	20	19.91	25.88
MM2/5	Al_2O_3	80	79.24	74.39
	SiO_2	20	20.76	20.93
MM2/6	Al_2O_3	80	78.39	73.09
	TiO_2	15	16.32	16.49
	P_2O_3	5	5.30	6.15
MM2/7	Al_2O_3	80	81.08	76.15
	TiO_2	15	14.07	13.88
	ZrO_2	5	4.85	7.81
MM2/8	Al_2O_3	80	77.67	73.94
	P_2O_5	10	10.98	13.55
	ZrO_2	10	11.35	6.66
MM2/9	Al_2O_3	80	80.12	72.18
	TiO_2	10	9.93	10.62
	ZrO_2	5	4.80	7.46
	P_2O_5	5	5.15	5.84
MM2/10	Al_2O_3	80	79.47	75.24
	P_2O_5	10	10.60	9.64
	SiO_2	10	10.93	11.04
MM2/11	Al_2O_3	80	79.85	73.77
	ZrO_2	10	9.56	8.04
	SiO_2	10	10.60	12.63
MM2/12	Al_2O_3	80	79.17	65.12
	SiO_2	10	10.76	8.73
	ZrO_2	5	4.85	4.60
	P_2O_5	5	5.22	3.87

* Based on analyses :

Natrium aluminate	Al_2O_3	73.2 g/l
Titanyl sulphate	TiO_2	76.2 g/l
Zirconium sulphate	ZrO_2	184.0 g/l
Calgon	P_2O_5	98.9 g/l
Water glass	SiO_2	68.0 g/l

Precipitation Process Documents

Acidic precipitation to a final pH of 6

Sample	Precipitation Time [min]	NaOH+Na$_2$O$_3$ Consumption [ml]	First Filtration Time [min]	First Washing Time [min]	Second Filtration Time [min]	Second Washing Time [min]
MM1A/1	58	2730	22	20	56	130
MM1A/2	63	2550	17	17	61	111
MM1A/3	51	2040	17	11	48	84
MM1A/4	60	2340	22	14	62	88
MM1A/5	48	1890	12	12	43	74
MM1A/6	64	2540	18	15	55	76
MM1A/7	66	2650	6	10	52	75
MM1A/8	52	2220	13	11	44	46
MM1A/9	62	2480	14	10	44	75
MM1A/10	53	2080	11	9	39	49
MM1A/11	56	2180	12	11	42	67
MM1A/12	51	1960	11	12	36	57

Acidic precipitation to a final pH of 8

MM1B/1	71	2800	16	10	40	44
MM1B/2	71	2740	13	6	33	45
MM1B/3	56	2220	12	9	28	56
MM1B/4	65	2580	13	8	36	45
MM1B/5	53	2070	11	4	29	28
MM1B/6	67	2670	14	10	41	42
MM1B/7	68	2780	14	8	46	47
MM1B/8	62	2420	17	8	47	53
MM1B/9	69	2680	13	4	32	33
MM1B/10	55	2180	10	6	25	50
MM1B/11	61	2330	10	4	24	29
MM1B/12	56	2160	9	5	27	39

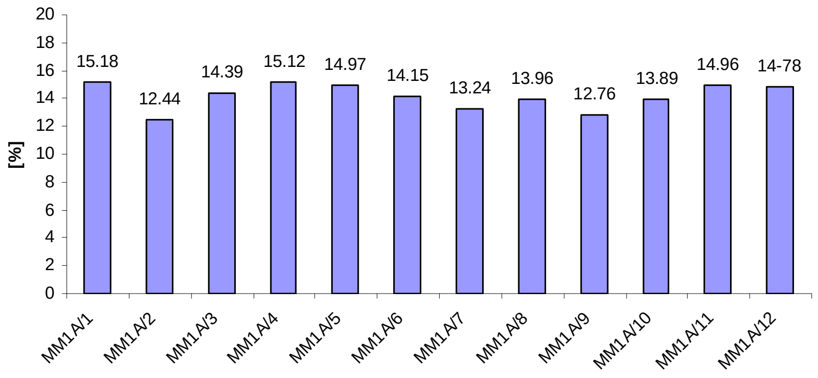
Precipitation Process Documents

Basic precipitation to a final pH of 7

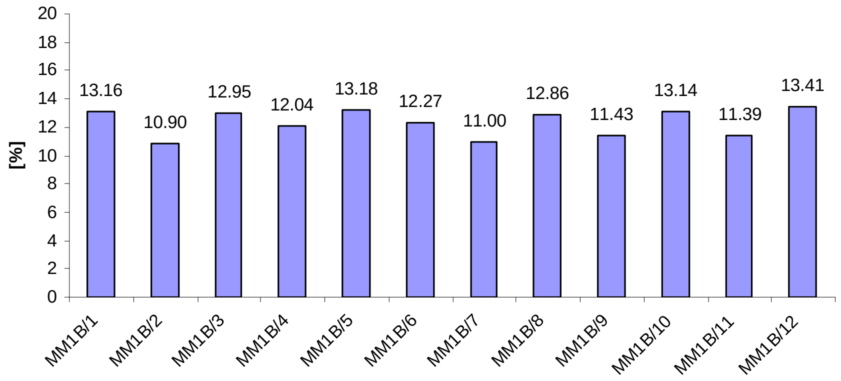
Sample	**Precipitation Time [min]**	**H_2SO_4 Consumption [ml]**	**Filtration Time [min]**	**Washing Time [min]**
MM2/1	41	1600	7	16
MM2/2	34	380	18	54
MM2/3	56	1540	45	200
MM2/4	52	1250	7	11
MM2/5	61	1350	13	35
MM2/6	36	650	16	76
MM2/7	39	750	11	31
MM2/8	44	1260	23	118
MM2/9	38	910	10	30
MM2/10	62	1400	12	39
MM2/11	49	1350	18	26
MM2/12	56	1350	16	48

Solids Contents of Wet Cakes

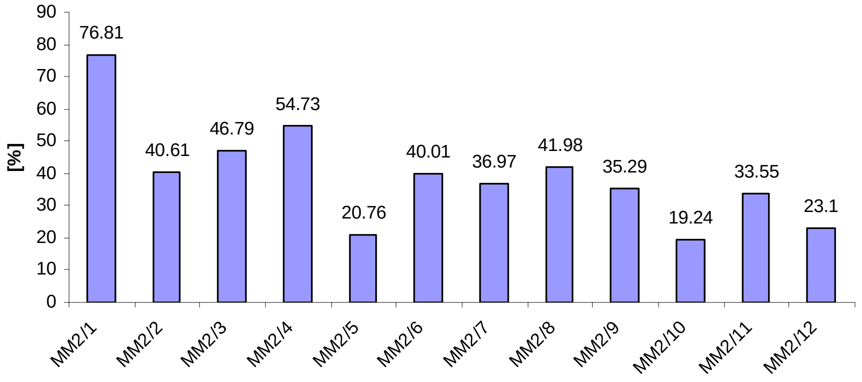
Acidic Precipitation to a End pH of 6



Acidic Precipitation to a End pH of 8



Basic Precipitation to a End pH of 7



APPENDIX 4

Crystallinity of the Samples

Sample Code	Crystalline	Morphology
MM1A/1	Amorphous	
MM1A/2	Amorphous	
MM1A/3	Amorphous	
MM1A/4	Amorphous	
MM1A/5	Amorphous	
MM1A/6	Amorphous	
MM1A/7	Amorphous	
MM1A/8	Amorphous	
MM1A/9	Amorphous	
MM1A/10	Amorphous	
MM1A/11	Amorphous	
MM1A/12	Amorphous with crystalline elements	AlO(OH) elements
MM1B/1	Amorphous with crystalline elements	AlO(OH) elements
MM1B/2	Amorphous with crystalline elements	AlO(OH) elements
MM1B/3	Amorphous with crystalline elements	AlO(OH) elements
MM1B/4	Amorphous with crystalline elements	AlO(OH) elements
MM1B/5	Amorphous with crystalline elements	AlO(OH) elements
MM1B/6	Amorphous with crystalline elements	AlO(OH) elements
MM1B/7	Amorphous with crystalline elements	AlO(OH) elements
MM1B/8	Amorphous with crystalline elements	AlO(OH) elements
MM1B/9	Amorphous with crystalline elements	AlO(OH) elements
MM1B/10	Amorphous with crystalline elements	AlO(OH) elements
MM1B/11	Amorphous with crystalline elements	AlO(OH) elements
MM1B/12	Amorphous with crystalline elements	AlO(OH) elements
MM2/1	Crystalline	$Al(OH)_3/Al_2(OOH)_2$
MM2/2	Crystalline	$Al(OH)_3$
MM2/3	Crystalline	$Al(OH)_3$
MM2/4	Crystalline	Al_2O3*3H2O/AlO(OH)
MM2/5	Amorphous with crystalline elements	$Al(OH)_3$ elements
MM2/6	Crystalline	$Al(OH)_3$
MM2/7	Crystalline	$Al(OH)_3$/AlO(OH)
MM2/8	Crystalline	$Al(OH)_3$
MM2/9	Amorphous with crystalline elements	$Al(OH)_3$/AlO(OH)
MM2/10	Crystalline	$Al(OH)_3$ elements
MM2/11	Crystalline	$Al_2O_3/Al(OH)_3$
MM2/12	Amorphous with crystalline elements	$Al(OH)_3$ elements

APPENDIX 5

Chemical Composition of Intermediate Samples

Sample code	**MM2/2/1 IS**	**MM2/2/2 IS**	**MM2/4 IS**	**MM2/5 IS**	**MM2/6 IS**	**MM2/7 IS**
Sample content	**Al_2O_3 80%** **TiO_2 20%**	**Al_2O_3 80%** **TiO_2 20%**	**Al_2O_3 80%** **ZrO_2 20%**	**Al_2O_3 80%** **SiO_2 20%**	**Al_2O_3 80%** **TiO_2 15%** **P_2O_5 5%**	**Al_2O_3 80%** **TiO_2 15%** **ZrO_2 5%**
Made	19.11.2008	19.11.2008	20.11.2008	20.11.2008	21.11.2008	22.11.2008
Uniquant:						
Na_2O %	33.15	23.33	50.02	71.34	27.59	25.36
Al_2O_3 %	30.39	48.91	35.00	23.41	46.94	49.46
SiO_2 %	0.01	0.08	0.17	4.68	0.03	0.05
P_2O_5 %	<	<0.01	<	0.02	1.57	<
SO3 %	28.61	16.93	0.16	0.12	15.07	13.53
K_2O %	<0.01	<0.01	0.09	0.16	0.01	0.01
TiO_2 %	7.68	10.66	0.04	0.02	8.69	7.07
Fe_2O_3 %	<0.01	0.01	<0.01	0.01	<0.01	0.01
ZrO_2 %	<0.01	<	7.64	0.04	0.01	3.41
Nb_2O_5 %	<0.01	0.01	0.02	<0.01	<0.01	<
Sb_2O_3 %	<	<	<	<	<	<

Sample code	**MM2/8 IS**	**MM2/9 IS**	**MM2/10 IS**	**MM2/11 IS**	**MM2/12 IS**
Sample content	**Al_2O_3 80%** **ZrO_2 10%** **P_2O_5 10%**	**Al_2O_3 80%** **TiO_2 10%** **ZrO_2 5%** **P_2O_5 5%**	**Al_2O_3 80%** **SiO_2 10%** **P_2O_5 10%**	**Al_2O_3 80%** **SiO_2 10%** **ZrO2 10%**	**Al_2O_3 80%** **SiO_2 10%** **P_2O_5 5%** **ZrO2 5%**
Made	22.11.2008	22.11.2008	24.11.2008	24.11.2008	25.11.2008
Uniquant:					
Na_2O %	47.90	30.23	61.84	61.55	52.67
Al_2O_3 %	39.23	43.07	29.41	27.28	35.92
SiO_2 %	0.03	<	2.85	3.02	3.17
P_2O_5 %	5.89	1.56	5.64	0.04	2.91
SO3 %	0.87	13.91	0.11	0.04	0.04
K_2O %	0.02	0.01	0.04	0.10	0.05
TiO_2 %	0.12	6.04	0.02	0.01	0.01
Fe_2O_3 %	<0.01	<0.01	0.01	0.01	0.01
ZrO_2 %	2.47	4.03	<0.01	4.67	3.28
Nb_2O_5 %	<0.01	0.01	<0.01	0.01	<
Sb_2O_3 %	<	<	<	<	<

***The intermediate samples were taken after all the precipitate chemicals had been fed and before the feed of the sulphuric acid was started.**

Brightness and Tone Values

Acidic precipitations to a final pH of 6

MM1A	**/1**	**/2**	**/3**	**/4**	**/5**	**/6**	**/7**	**/8**	**/9/**	**10**	**/11**	**/12**
Brightness, L*	98.96	98.45	98.76	98.80	98.84	98.60	98.64	98.80	98.68	98.92	98.82	98.84
Tone, b*	1.21	1.85	1.09	1.37	0.94	1.44	1.53	1.04	1.40	1.06	1.27	1.11

Acidic precipitations to a final pH of 8

MM1B	**/1**	**/2**	**/3**	**/4**	**/5**	**/6**	**/7**	**/8**	**/9/**	**10**	**/11**	**/12**
Brightness, L*	98.55	97.34	98.95	98.35	98.51	97.76	97.19	98.55	98.32	98.52	98.30	97.95
Tone, b*	1.60	3.35	1.04	1.92	1.32	2.60	2.44	1.49	1.81	1.20	1.64	1.71

Basic precipitations to a final pH of 7

MM2	**/1**	**/2**	**/3**	**/4**	**/5**	**/6**	**/7**	**/8**	**/9/**	**10**	**/11**	**/12**
Brightness, L*	98.12	98.31	98.37	98.27	98.81	98.29	98.15	98.03	98.32	98.74	98.66	98.89
Tone, b*	2.86	3.08	2.20	2.25	1.65	2.91	3.15	3.07	2.25	1.85	2.09	1.55

APPENDIX 7

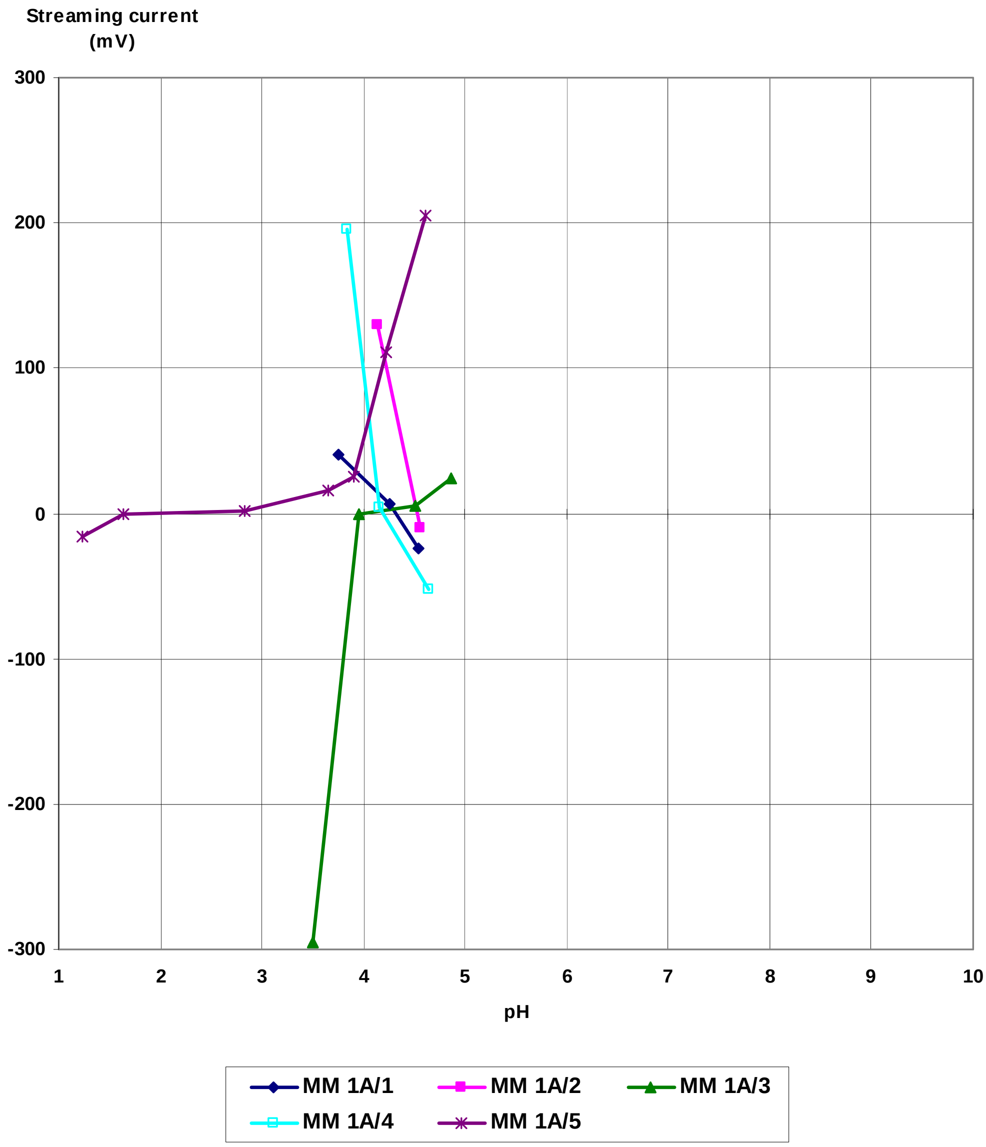
Surface Properties of the Samples

Sample Code	Oil Absorption [%]	Specific Surface [m^2/g]	Pore Volume [µl/g]	Pore Size [Å]	Isoelectric Point (IEP)
MM1A/1	81.0	94	234	49	4.3
MM1A/2	69.9	157	422	53	4.5
MM1A/3	130.6	203	716	69	4.0
MM1A/4	64.4	125	205	32	4.2
MM1A/5	99.4	157	551	69	1.6
MM1A/6	92.0	158	519	64	-
MM1A/7	84.6	142	310	42	-
MM1A/8	110.4	179	473	52	-
MM1A/9	90.2	142	317	44	-
MM1A/10	114.9	169	525	61	-
MM1A/11	79.1	137	319	46	-
MM1A/12	106.7	217	345	31	-
MM1B/1	35.0	17	41	48	-
MM1B/2	23.9	159	175	21	-
MM1B/3	128.8	250	645	50	-
MM1B/4	38.6	166	171	20	-
MM1B/5	57.0	193	309	31	-
MM1B/6	31.3	144	203	27	-
MM1B/7	31.3	164	193	23	-
MM1B/8	57.0	194	293	29	-
MM1B/9	49.7	202	272	26	-
MM1B/10	92.0	232	549	46	-
MM1B/11	47.8	200	235	23	-
MM1B/12	49.7	223	342	30	-
MM2/1	35.0	7	21	64	4.3
MM2/2	57.0	44	52	23	3.6
MM2/3	64.4	38	128	65	3.2
MM2/4	38.6	41	33	16	4.8
MM2/5	195.0	297	511	33	4.9
MM2/6	81.0	69	194	54	-
MM2/7	46.0	53	59	21	-
MM2/8	68.1	52	117	44	-
MM2/9	95.7	96	165	33	-
MM2/10	184.0	353	561	31	-
MM2/11	110.4	219	333	30	-
MM2/12	132.5	207	373	35	1.5

The Effect of Wet Grinding on Particle Size

	Particle Size, d(0.1)/ d(0.5)/ d(0.9)µm		
Sample code	**30 minutes**	**2 hours**	**4 hours**
MM1A/1	7.21/28.10/56.69	5.01/13.60/26.13	3.43/7.89/15.38
MM1A/2	5.76/25.69/74.39	4.09/11.06/27.88	3.22/7.11/14.77
MM1A/3	5.61/24.95/57.74	4.45/13.43/28.36	4.05/9.11/17.98
MM1A/4	7.11/38.61/84.34	4.30/14.93/30.87	3.37/8.02/16.13
MM1A/5	4.75/20.17/64.67	4.24/9.39/19.36	4.15/8.65/16.93
MM1B/1	5.13/21.19/58.09	3.69/11.50/26.71	3.04/8.09/17.64
MM1B/2	7.40/49.94/119.36	19.33/150.40/281.55	3.58/82.59/222.53
MM1B/3	4.85/31.90/123.69	3.62/13.87/32.74	2.96/8.46/18.93
MM1B/4	4.71/32.01/94.73	4.51/29.16/94.29	3.11/16.01/42.44
MM1B/5	4.13/20.87/75.26	2.86/8.57/24.95	2.35/5.99/13.91
MM2/1	15.09/36.44/75.97	1.09/20.55/39.31	0.81/11.47/24.99
MM2/2	8.12/27.78/66.89	0.85/12.49/26.84	0.64/4.85/14.55
MM2/3	7.29/44.05/101.98	3.94/25.55/58.59	1.08/14.91/34.29
MM2/4	14.48/31.75/60.62	1.04/18.62/36.10	0.78/10.33/23.07
MM2/5	4.27/14.82/39.66	1.18/6.87/18.88	0.76/4.10/12.77

Isoelectric Point of Acidic Precipitated Samples



Results of Reference Precipitation

Sample code		**MM0B**
Sample name		Al_2O_3 100%
Made		16.12.2008
1. Filtration	min	5
1. Washing	min	13
2. Filtration	min	2
2. Washing	min	20
Solids content	%	12.63
pH (wet cake)		6.6
Crystalline / Amorphous		Amorphous
Morfology		AlOOH elements
Brightness	L*	98.89
Tone	b*	0.96
Sp. resistance	kohmcm	0.2
pH (dried sample)		4.6
Oil absorption	%	99.6
Uniquant:		
Na_2O	%	0.05
Al_2O_3	%	88.25
SiO_2	%	0.04
P_2O_5	%	<0.01
SO3	%	11.48
K_2O	%	<
TiO_2	%	0.12
Fe_2O_3	%	0.01
ZrO_2	%	<0.01
Nb_2O_5	%	<0.01
Sb_2O_3	%	<
Sp. surface area	m^2/g	103
Pore volume	10^{-3} ml/g	128
Pore size	Å	24