

Precipitation of reactive aluminium hydroxide from an acidic aluminium sulphate solution by addition of sodium hydroxide

Emilia Andersson, Henrik Hansson

Department of Chemical Engineering II, University of Lund, P.O. Box 124, S-22100 Lund, Sweden

The goal of the present thesis was to study the possibilities of producing an aluminium hydroxide, which would easily dissolve in hydrochloric acid. Furthermore, the product should be easy to dewater. In the experiments, which were made batch-wise, a 50% sodium hydroxide was used to accomplish the precipitation. The precipitation of aluminium hydroxide is a dynamic process that depends on many parameters, e.g. the stirring rate and base addition rate. A factorial experiment showed that stirring rate and base addition rate were the factors of largest influence on filterability. A high stirring rate and a slow base addition rate improved the filterability. The method used in this master thesis could most likely be used in the production of aluminium hydroxide.

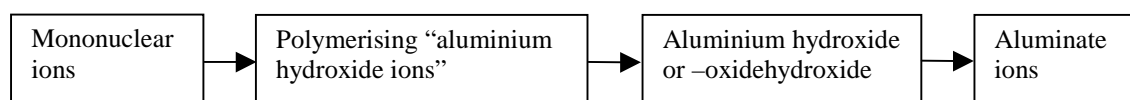
OBJECTIVE

The main target of this study was to investigate the process parameters controlling the precipitation of aluminium hydroxide. The optimal precipitation product has a high dry content and is easy to dissolve in a hydrochloric acid under mild conditions, i.e. normal temperature and pressure (NTP).

BACKGROUND

The company Kemira Kemi AB situated in Helsingborg, Sweden, produces precipitation- and flocculation chemicals used in waste- and freshwater plants. The active substances are either iron or aluminium, and this study only deals with matters concerning the latest mentioned. The raw material is aluminium hydroxide, which is boiled at elevated pressure with hydrochloric acid to produce polyaluminium hydrochloric acid. If another, more reactive, raw material could be used some of the process expenses could be eliminated.

Although thorough, the literature study gave little information about how to best precipitate aluminium hydroxide from an acidic aluminium solution. There is an important difference compared to the Bayer process, in which aluminium hydroxide is precipitated from a basic aluminate solution, and this is shown in the picture below where pH is increasing from left to right.



If base is added to an acidic solution, precipitation will occur because the solubility of aluminium hydroxide is very low between pH 4 and pH 9.5. The pathways and products of this reaction are not well known, but the stable product at NTP is gibbsite, $\text{Al}(\text{OH})_3$. The critical factor is the time needed to reach equilibrium, and in the meantime different form of unstable "aluminium hydroxide ions", such as, for example, $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}[(\text{OH})_5\text{Al}_2]_n^{+3+n}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ or $\text{Al}_{14}(\text{OH})_{34}^{8+}$, may be formed. These polymerise readily and the gels are very hard to dewater. Many authors agree that process parameters like temperature, stirring

rate etc. control the precipitation product. It is a known fact that smaller particles give rise to a product that is more difficult to dewater.^{1 2 3}

EXPERIMENTAL PROCEDURE

The experimental work was divided into two main parts; a preliminary investigation followed by a statistically designed study.

The original acidic aluminium solution contained 0.7% aluminium in the form of $\text{Al}_2(\text{SO}_4)_3$ and 0.7% H_2SO_4 as free acid. To this solution 50%[‡] NaOH were added and the reaction was carried out in a 2 l. LDPE-vessel from Kautex Textron, and this container were kept in a heated water bath to ascertain constant temperature. The stirrer, RW 20, and the revelation counter, DMZ1, were both from Janke & Kunkel IKA-WERK.

Primarily the filterability was studied. The time needed to filter 100 ml was measured, and the filterability was calculated by the formula below.

$$\text{Filterability} = 100/t$$

In the preliminary study of the filterability, the dry content, the particle size distribution and the x-ray diffraction patterns were investigated for different experimental situations. Parameters varied were the amount of base added, the temperature and the retention time.

Factorial design

Six different factors; temperature, stirring rate, usage of seed crystals, base quota, retention time and base injection rate, were varied in a 2^{k-p} experiment. In this kind of experiment main effects are confounded with interaction effects.

	FACTOR	LOW	HIGH
A	Temperature, [°C]	40	60
B	Stirring rate, [min^{-1}]	60	360
C	Seed crystals, [g/1.5 kg]	0	50
D	Base quota	2.95	3.05
E	Retention time, [min]	20	180
F	Base injection rate	Burette	instant

Table 1 – The factors and the levels used in the factor experiment

Response surface experiment

As a result of the factor experiment two factors were more thoroughly investigated, the stirring rate and the base injection rate. A response surface experiment was carried out to find a mathematical correlation between the stirring rate, the base injection rate and the filterability and possibly determine the optimum conditions with respect to the filterability. Nine experiments were done with different stirring rates (100, 250 or 400 rpm) and different times of base injection (1.5, 17 or 28 min). Particle size distribution, pH of the final solutions, reactivity, X-ray diffraction and the dry content was studied.

[‡] weight -%

RESULTS AND DISCUSSION

Preliminary experiment

- It seemed like the filterability and the dry content did not depend on the temperature. It was clear though, that a higher amount of base added lowered the filterability.
- The particle size distribution seemed to contain three, more or less, distinct fractions, see figure 1. There were some indications that the particle properties were more important than the size for the filterability. The dry contents of the particles were very low, which indicate that they had high affinity for water. A possible explanation of the different filterabilities could be that the affinities varied and the more hydrophobic were possibly easier to dewater.
- The x-ray diffraction patterns showed that the particles were very amorphous. It could be assumed that solutions containing more sodium hydroxide had a more crystalline structure. Possibly the more crystalline particles contained pseudo bohemite. The x-ray diffractograms showed broad bands suggesting that either that the crystallites are very small or the distances between the crystal layers varied.
- In the vessels pH changed with time, as shown in figure 2. The reason for this behaviour could not be explained, but the chemical reactions certainly include the accepting and donation of hydrogen ions.

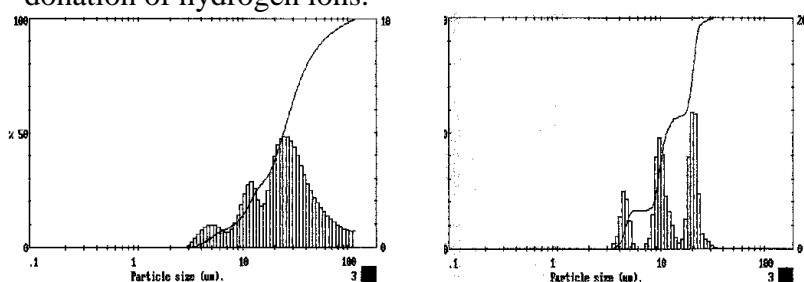


Figure 1 - Examples of the particle size distribution

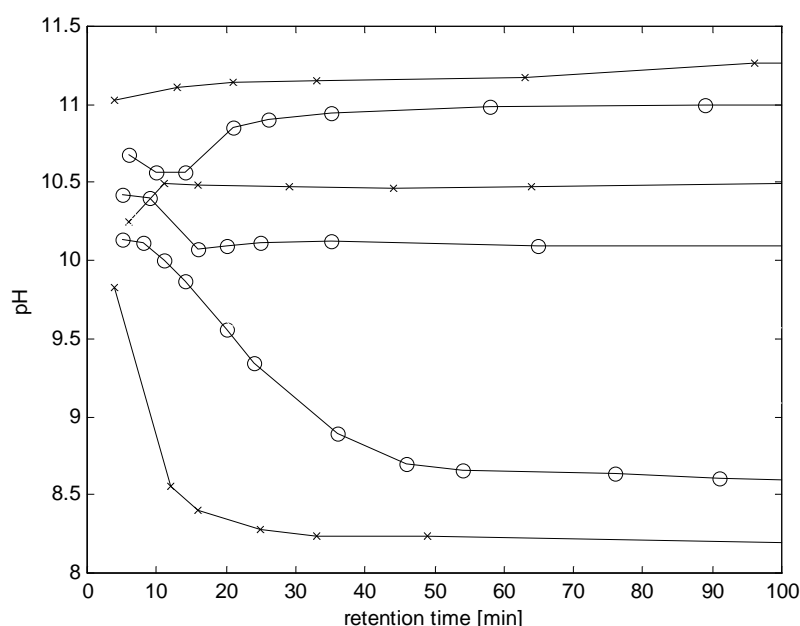


Figure 2 - The influence of retention time on pH

Factorial design

In table 2 the variation of the factors and the resulting filterability is shown.

The effects of the different factors are shown in table 3[‡]. As no measurement of the standard deviation for the effects has been made, it is convenient to use the smallest value, which in this case is 0.39. It is small compared to 8.4 and 4.9, these can therefore be considered significant.

It is evident that a high stirring rate and low base injection rate will increase the filterability, a lower base quota will also have this effect. The retention time and the temperature have no apparent influence on the filterability.

EXP.	A	B	C	D	E	F	FILTERABILITY [ml/min]
1	-	-	-	+	+	+	4.8
2	+	-	-	-	-	+	11
3	+	+	-	+	-	-	29
4	-	+	-	-	+	-	40
5	-	-	+	+	-	-	9.1
6	+	-	+	-	+	-	17
7	-	+	+	-	-	+	20
8	+	+	+	+	+	+	20

Table 2 - Scheme of the factors and result of the filterability

FACTOR	EFFECTS
A	0.39
B	8.4
C	-2.3
D	-3.1
E	1.6
F	-4.9

Table 3 - Influence of each factor on the filterability

Response surface experiment

The data of the response surface experiment was best fitted to a linear model which can be found below. As a consequence of this equation, that is a plane in space, it is impossible to say where an optimum can be found. However, within the area where the experimental data was collected higher stirring rate and longer base addition time means better filterability.

$$\text{Filterability} = -3.0352 + 4.2419 \cdot r + 0.4808 \cdot t$$

[‡] Calculation of the influence of factor A:

$$\text{Effect}_A = \frac{1}{8} (-4.8 + 11 + 29 - 40 - 9.1 + 17 - 20 + 20)$$

CONCLUSIONS

The result of this master thesis suggests that stirring rate and base addition rate are the factors with largest influence on filterability. A high stirring rate and a slow base addition rate improves the filterability. Perhaps surprisingly, there was no correlation between filterability and particle size, suggesting that other properties than merely the particle size decides the filterability. No conclusions could be drawn regarding the reactivity of the produced aluminium hydroxide.

The method used in this master thesis could most likely be used in the production of aluminium hydroxide. However, further studies on the reactivity should in that case be performed.

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