DOI: 10.61458/jepm2301030P
UDC: 669.712

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Journal of
Engineering & Processing Management

ORIGINAL SCIENTIFIC PAPER

The influence of process parameters on the morphological characteristics of fine precipitated hydrate

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Abstract

In this paper, the influence of process parameters on the morphological properties of fine precipitated hydrate was examined. The research was conducted with the aim of synthesizing fine precipitated aluminum hydroxide from the aluminate solution obtained by the Bayer process. Fine precipitated hydrates obtained in this way are mostly used in the non-metallurgical industry. The synthesized fine precipitated hydrate should comply with certain quality requirements such as granulometry (average particle diameter), purity, specific surface area, whiteness, etc. This paper shows the influence of certain technological parameters, namely the initial precipitation temperature, the amount and specific surface area of the seed, the influence of the NaOH/Al(OH)3 molar ratio on the characteristics of the synthesized fine precipitated hydrate in terms of the specific surface area, mean diameter and morphology of the obtained particles.

Keywords: analysis, hydrate, process, particle

1. INTRODUCTION

Alumina (aluminum oxide) can be obtained using alkaline, acidic, and electrochemical processes. The largest number of factories work according to the Bayer process (alkaline), while other processes are of less importance. For more than a century, the conventional Bayer process has been used to produce alumina (Al_2O_3) from the bauxite ore (Sonthalia, Behara, Kumaresan, & Thakre 2013). The Bayer process is based on the fact that the sodium hydroxide dissolves the aluminum oxide in the bauxite, and the other components are left behind in the form of red mud as an insoluble residue.

The simplified reaction could be written as follows:

$(Al_2O_2,\ Fe_2O_3,\ SiO_2,\ TiO_2)^{+}2NaOH\rightleftarrows\ 2AlNaO_2+ H_2O\ +\ (Fe_2O_3+\ SiO_2+\ TiO_2)$

When the red mud is removed from the sodium aluminate solution, it is necessary to perform the reverse operation,*i.e.*, to get aluminum oxide back from the sodium aluminate solution. This process takes place under certain conditions as follows:

$2AlNaO_2+\ 4H_2O\rightleftarrows\ Al2O3\bullet\ 3H_2O\ +\ 2NaOH$

As can be seen from the formula, aluminum trihydroxide (ATH) was obtained. Precipitation of aluminum hydroxide from a supersaturated solution of sodium aluminate is known as an essential production step in the Bayer process. The three fundamental phenomena in the precipitation of aluminum hydroxide in the Bayer process include nucleation, growth, and agglomeration. Fresh fine grains are formed by nucleation (Lee et al. 2009). Crystal growth is a process in which the dissolved matter is precipitated from a supersaturated solution on the crystal surface. The process of agglomeration can be represented as a process in which particles collide and adhere to each other, creating larger particles. Crystallization is the formation of solid particles within a homogeneous phase. It usually implies a slower process in which molecules come out of solution and form, molecule by molecule, a crystal structure. Precipitation generally refers to the relatively rapid formation of a poorly soluble solid phase from a liquid phase. The process itself begins with the creation of nuclei (the smallest crystal cores),

from which crystals of different granulometric properties are formed, depending on the crystallization method.

The crystallization process consists of several intermediate phases, the description of which has a large number of theoretical bases.

In general, it can be said that crystallization begins with the nucleation of impurity particles in the solution (heterogeneous nucleation) or the creation of embryos (homogeneous nucleation) (Li, Addai-Mensah, Thomas, & Gerson 2005; Mirzaei, Noaparast, & Abdollahi 2021). The process continues with the growth of the created nuclei and the formation of crystals, and ends with the ageing of the sediment. The ageing of the precipitate results in a single crystal in equilibrium with the solution; however, if the precipitation is followed for some finite time, sedimentation is the last stage of the process.

Nucleation represents the creation of new $Al(OH)_3$ particles from supersaturated aluminate solutions.

Nucleation is the first step in the crystallization process. With favorable conditions (increasing the concentration of particles) a critical nucleus can be formed, which continues to grow by a spontaneous process.

Primary nucleation occurs in the absence of solid particles in the solution and represents the spontaneous formation of crystals from the solution, while secondary nucleation is conditioned by the presence of crystallization centers (seed). Considering that aluminate solutions decompose slowly, the seed is used as a process accelerator. The seed is pre-precipitated $Al(OH)_3$. Secondary nucleation occurs due to the fragmentation of crystals present in a supersaturated solution, which must be sufficiently large and irregular. Secondary nuclei decrease the nucleation activation energy.

The number of nuclei created affects the size of the crystal, that is, a smaller number of nuclei results in larger crystals, while a larger number of nuclei results in smaller crystals. The creation of a large number of nuclei is favored by rapid cooling, vigorous mixing, high temperature and low molecular weight of the dissolved substance.

Unlike nucleation, agglomeration represents the sticking of smaller particles into larger aggregates and, together with the growth of crystals, it is the main factor in the consolidation of the resulting $Al(OH)_3$. "Ilievski and White" say that agglomeration occurs in the initial period of crystallization, when crystal growth is almost negligible.

They also believe that agglomeration takes place by forming weakly bound flocs (clusters of particles) and, if they survive, thanks to the growth of the particles, they turn into stable aggregates.

This paper is based on the examination of the morphology and process parameters that influence the characteristics of fine precipitated aluminum hydroxide. Fine precipitated hydrate (FPH) is used in different industries as an environmentally friendly filler and flame retardant for plastic and rubber materials, for paper, cardboard, paints, and as an integral part of ceramics and polishing compounds (Rothon & Hornsby 2014; Sauerwein 2007; Xiao & Kibble 2008). Fine precipitated hydrate has significant applications and is known as one of the most important flame retardants used in the world (Yew, Ramli Sulong, Yew, Amalina, & Johan 2015).

2. EXPERIMENTAL

In the experimental part of this paper, the influence of process parameters on the characteristics of fine precipitated hydrate was examined. The influence of the change in the process temperature, the change in the modulus (αk) of the initial aluminate solution, and the influence of the amount and specific surface area of the seed were examined as the variables,while the other parameters were fixed in order to monitor more easily and more precisely the influence of only one of the variables and reach a relevant conclusion more easily. Samples of fine precipitated hydrate obtained in the laboratory conditions of the alumina factory "ALUMINA" d.o.o. Zvornik, Bosnia and Herzegovina, were used in the paper. The raw materials used in production are process aluminates and seeds obtained in current production.

Experimental work was carried out using standard laboratory ware, A.R. chemicals, instruments and methods of the research laboratory at "Alumina" d.o.o. Zvornik and one part at the Faculty of Technology and Metallurgy in Belgrade.

The following factors were examined: the influence of the temperature of the solution, the influence of the amount and surface area of the seed and the influence of the caustic modulus on the average particle size, specific surface area, and the degree of decomposition (Qian et al. 2013; Xue et al. 2019; Zolfaghari, Rezai, Bahri, & Mahmoudian 2020).

Also, scanning electron microscopy (SEM) of the samples was performed in order to observe the differences in the morphological characteristics of the hydrates.

In this paper, the distribution of particle sizes and the value of the mean diameter were determined using the laser diffraction method in the laboratory of the factory on the device CILAS 1090 LIQUID, according to the standard method ISO 13320 (Rhodes 2008; Stojanović, Marković, & Uskoković 2010).

The specific surface area of fine precipitated hydrate samples (The Brunauer, Emmett and Teller (BET) theory) was determined on a GEMINI VII device in the factory's laboratory (Hwang & Barron 2011).

The caustic modulus, αk, was calculated according to the Moving Average (MA) model, the Autoregressive (AR) model, 003.

The principle of this method is computational. The caustic modulus (αk) is calculated according to the formula:

$$\alpha_k = \frac{g/dm^3 Na_2O_k x mol.mas.Al_2O_3}{g/dm^3 Al_2O_3 x mol.mas.Na_2O_k}$$

SEM photos of the samples were taken at the Faculty of Technology and Metallurgy in Belgrade, on the MIRA3 TESCAN device, at a voltage of 20 kV and a magnification of 50.000 times (Mohammed & Abdullah 2018).

The experiments were performed by monitoring the influence of the initial temperature, the initial modulus αk and the specific surface area and amount of seed on the mean diameter of the particle, the specific surface area of the particle and the degree of decomposition.

The temperature ranged from 40 to 60 °C, with a constant amount of seed, over 24 and 48 h. The initial modulus $\alpha_k$ranged from 1.26 to 1.6, at a constant initial temperature of 40 °C.

The amount and specific surface of the seed ranged from 50.22 to 354.3 m^2/L, at a constant initial temperature of 40 °C.

3. RESULTS AND DISCUSSION

3.1. Influence of initial temperature

Temperature is one of the most important process parameters in every chemical-technological process, which is also the case in the production and synthesis of aluminum hydroxide.

The temperature of the aluminate solution, with other conditions unchanged, shows an affects both the rate of decomposition and the quality of the obtained aluminum hydroxide.

In this first part of the examination of process parameters, tests were performed at a constant synthesis temperature, at the isothermal conditions during the entire decomposition process.

In the first set of experiments, the dependencies of the mean diameter of the particles, the specific surface area of the particles, and the degree of decomposition depending on the initial temperature of the process were monitored. Based on the experimental data, dependency graphs were drawn.

The attached graph clearly shows the decrease in the average diameter of the particle with the decrease of the initial temperature of the synthesis from 60 to 40 °C, where the lowest values of the average diameter are exactly at the temperature of 40 °C.

The trend of increasing the specific surface area of fine precipitated hydrate with decreasing of the initial temperature is clearly seen in the attached figure, where the highest value is at the lowest temperature.

As the temperature decreases, there is a sudden increase in decomposition with a decrease in the synthesis temperature from 60 to 50 °C, and, with a further decrease to 40 °C, there is still an increase in % decomposition, but much slower, as can be seen in the attached figure.

3.2. Influence of initial molar ratio α_k

Caustic modulus (α_k) is another parameter monitored in this paper. As in the case of temperature, the dependences of the mean diameter of the particles, the specific surface and the degree of decomposition in relation to the caustic modulus were monitored.

With decreasing in the caustic modulus of the initial aluminate solution, a decrease in the mean particle diameter of the formed fine precipitated hydrate is evident and is the lowest at the caustic modulus α_k=1.26.

By reducing the caustic modulus of the initial aluminate solution, there is an increase in the specific surface area of the synthesized fine precipitated hydrate, and the highest values of the specific surface area were obtained at the lowest caustic modulus of the aluminate solution.

From the dependency graph, it is clearly visible that the degree of decomposition increases with a decrease in the caustic modulus. The highest percentage of decomposition was in the synthesis with the lowest modulus α_k.

3.3. Influence of the specific surface and seed amount

In the third set of experiments, the dependence on the amount and specific surface area of the seed was monitored. Analogous to the previous cases, the same dependencies represented on the y-axis were monitored.

With the increase in the specific surface area of the seed, the increase in the mean diameter of the synthesized fine precipitated hydrate is evident, and the lowest mean diameter was obtained by using the seed with the highest total specific surface area.

3.4. Scanning electron microscopy of samples

Based on the SEM images of the samples of the corresponding properties magnified 50,000 times, a clear difference can be seen for these 4 samples. For the first sample, (a), which has the smallest specific surface area and the largest mean diameter, the largest crystals are visible, with a regular hexagonal shape. Then, by increasing

Table 1. Values of parameters d_{50}, specific surface and degree of decomposition depending on the initial temperature of the process.

Sample	Initial Temperature (°C)	D_{50} after 48h of Decomposition (μ_m)	Specific surface (m^2/g)	Degree of Decomposition (%)
1	60	2.05	3.79	40.43
2	60	2.01	4.21	39.23
3	50	1.92	4.32	51.03
4	50	1.89	4.32	51.17
5	45	1.85	4.83	51.81
6	45	1.82	4.98	50.99
7	40	1.8	5.62	52.93
8	40	1.74	5.77	51.81

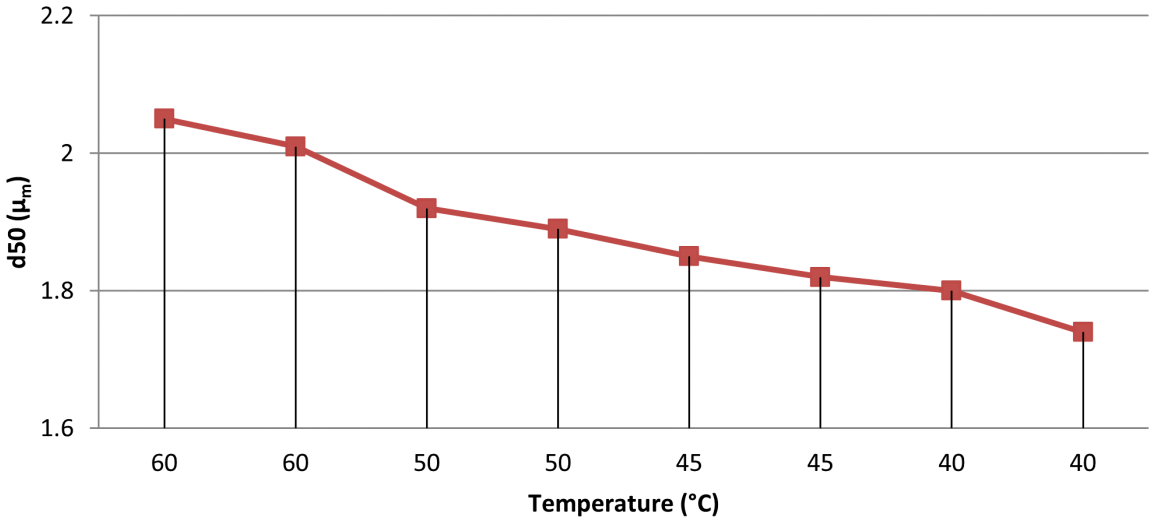

Figure 1. Dependence of the average particle size on the initial temperature after 48 h of decomposition.

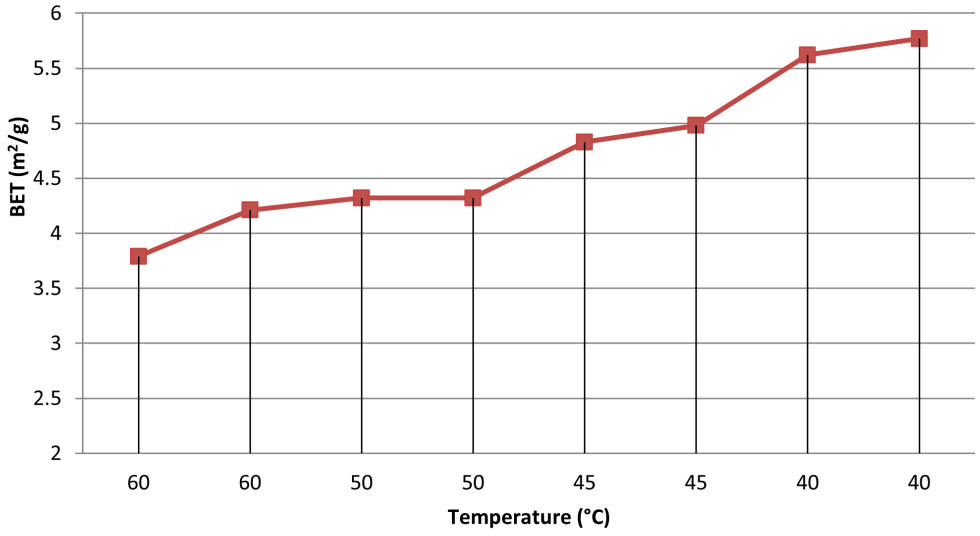

Figure 2. Dependence of the specific surface area of the particle on the initial temperature.

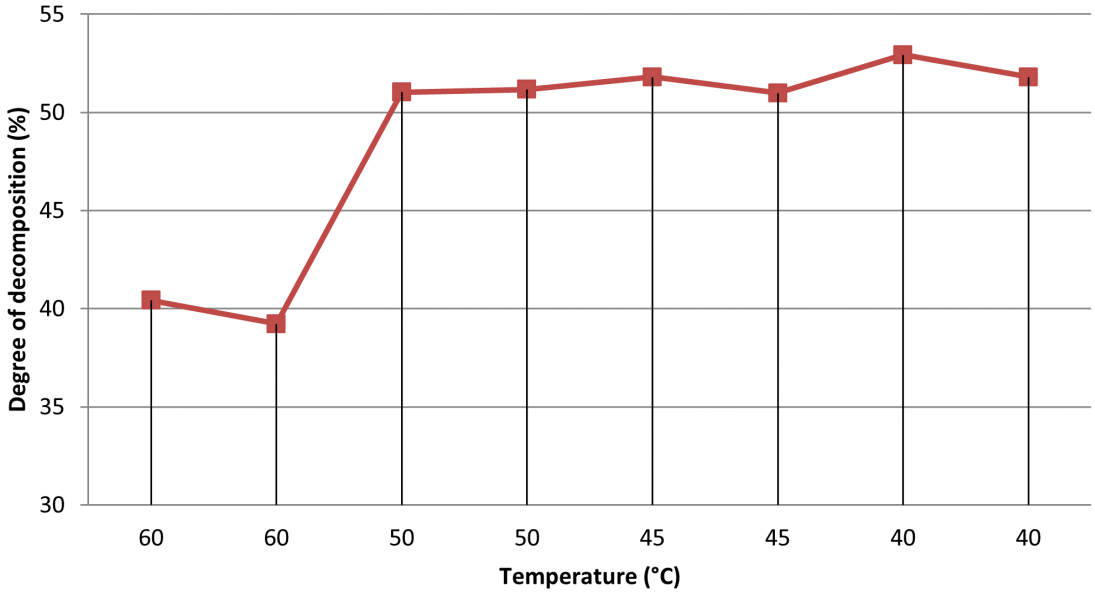

Figure 3. Dependence of the degree of decomposition on the initial temperature.

Table 2. Values of parameters D_{50}, specific surface and degree of decomposition depending on the initial caustic modulus αk.

Sample	Caustic modulus □k	D_{50} (μ_m)	Specific surface (m^2/g)	Degree of decomposition (%)
1	1.6	1.71	5.15	47.84
2	1.58	1.8	5.62	48.76
3	1.52	1.66	5.56	50.4
4	1.46	1.49	6.29	57.43
5	1.37	1.35	6.39	57.65
6	1.33	1.34	7.01	59.9
7	1.26	1.25	7.6	64.82

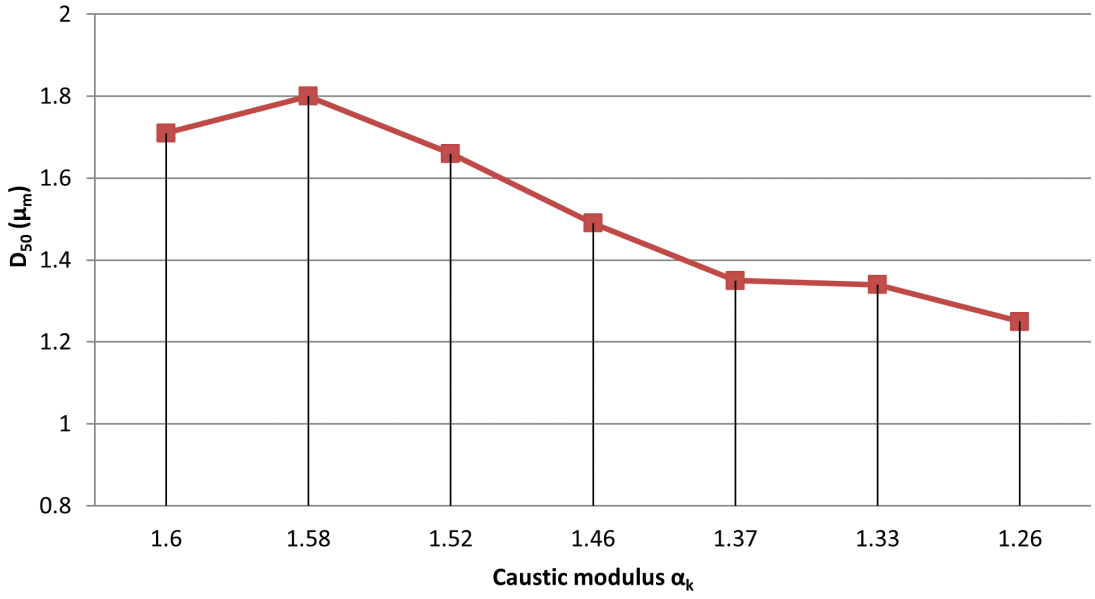

Figure 4. Dependence of the mean particle size (D_{50}) on the initial caustic modulus α_k.

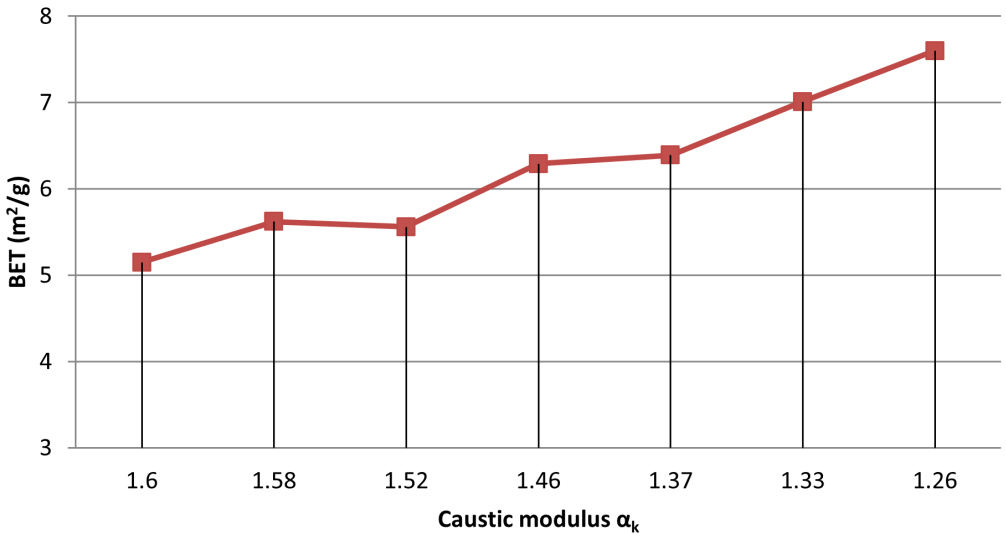

Figure 5. Dependence of the specific surface area of the particle on the initial caustic modulus α_k.

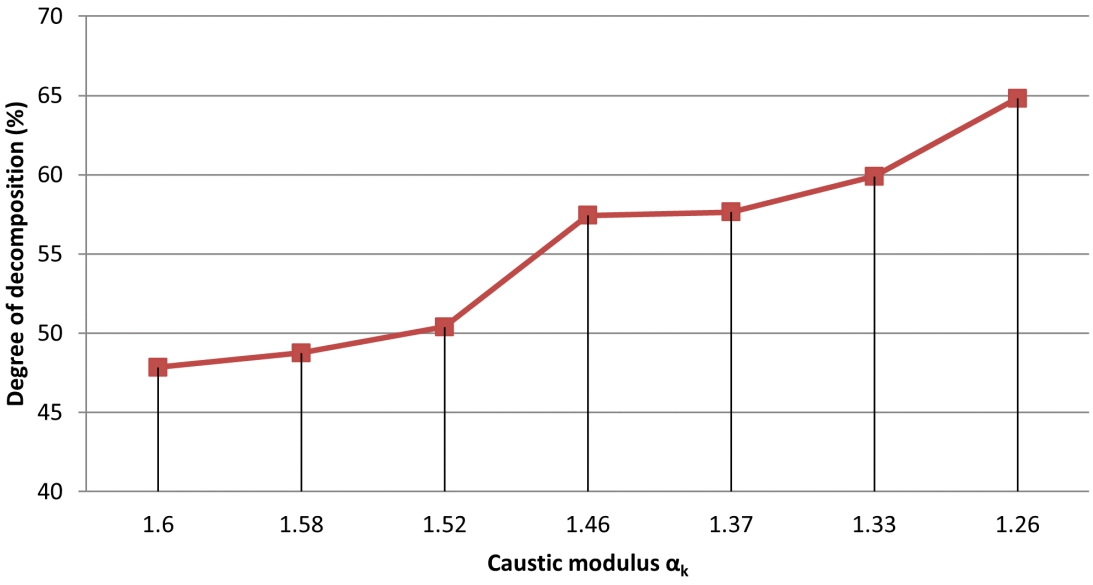

Figure 6. Dependence of the degree of decomposition on the initial caustic modulus α_k.

Table 3. Values of parameters D_{50}, specific surface and degree of decomposition depending on the amount and specific surface of the seed.

Sample	Specific surface of seed*c (m^2/l)	D_{50} (μ_m)	Specific surface (m^2/g)
1	50.22	3.15	5.21
2	83.7	2.42	5.21
3	133.92	2.64	5.15
4	167.4	2.25	5.62
5	203	1.41	7.2
6	271	1.77	7.58
7	354.3	0.86	9.77

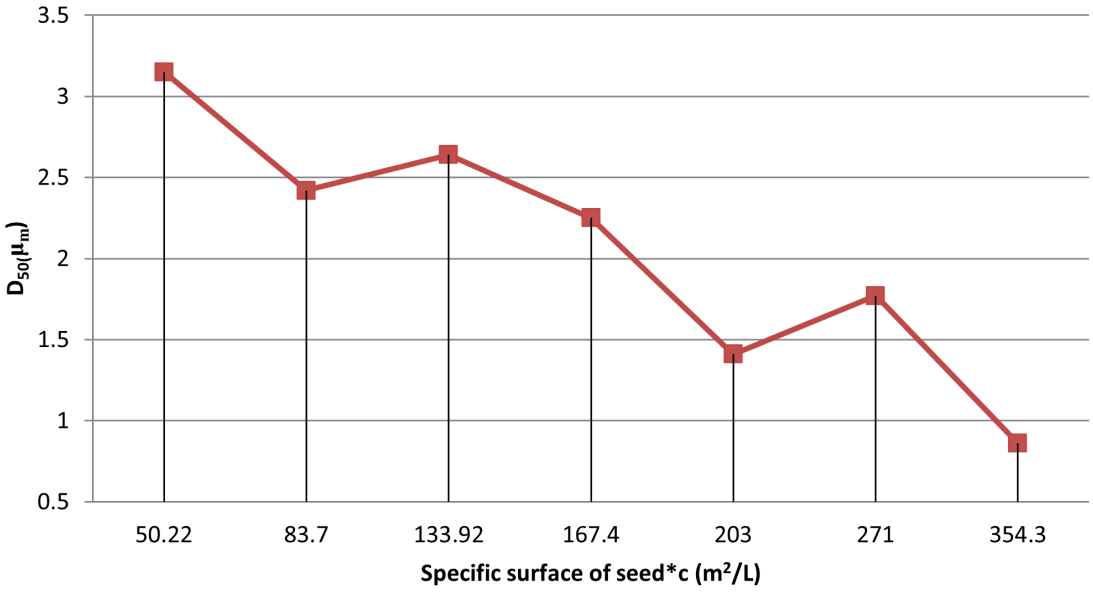

Figure 7. Dependence of the mean particle size on the amount and specific surface area of the seed.

the specific surface area, the shape of the crystal is more difficult to define, it is more irregular, built from multiple layers. It is clearly seen that the crystals decrease with the increase of the specific surface area. The last picture, (d), represents an SEM image of a sample obtained with the addition of the $Al_2(SO_4)_2$modifier. Crystals with a fluffy shape and a large specific surface area, but with a larger mean diameter of the particles, are noticeable.

The addition of modifiers leads to the creation of an amorphous state of the seed, and this type of seed crystal leads to the creation of the final product with an irregular shape and a large specific surface area.

4. CONCLUSIONS

Fine precipitated hydrate is a product with certain characteristics related to quality, granulometry, specific surface area, whiteness, etc. As such, this product is a raw material in other industry types. In this study, several parameters for fine-precipitated hydrate were monitored, and conclusions were drawn based on experimental data. Based on the performed experiments, it can be concluded that decreasing the temperature, reducing the caustic ratio and increasing the amount and surface area of the added seed favors the creation of a larger specific surface area and a reduction in the mean particle size, which leads to the production of products with better physicochemical characteristics.

Based on the dependency graph, it can be concluded that decreasing the temperature leads to a decrease in the size and mean diameter of the particle. Regarding

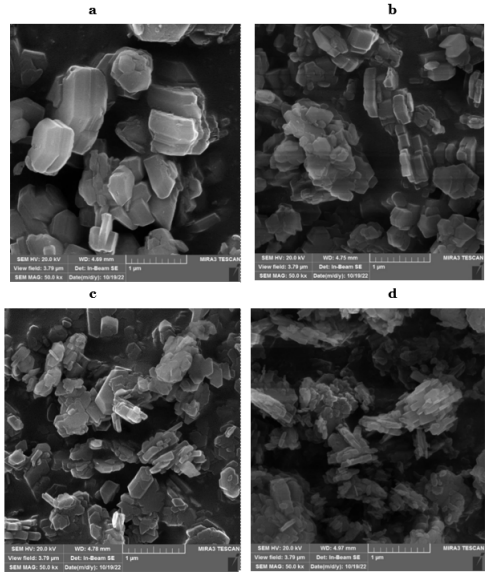

Figure 8. SEM micrographs showing (a) sample 1: BET=3.58 m^2/g; D_{50}=1.43 μ_m(b) sample 2: BET=9.91 m^2/g; D_{50}=1.4 μ_m(c) sample 3: BET=9.91 m^2/g; D_{50}=1 μ_m(d) sample 4: BET=12.96 m^2/g; D_{50}=1.37 μ_m.

the specific surface area of the particles, decreasing the temperature leads to a significant increase in the specific surface area. As expected, the degree of decomposition increases with decreasing temperature.

By reducing the caustic modulus of the initial aluminate solution, fine precipitated hydrates with a lower average diameter and larger specific surface are obtained, and everything is accompanied by an increase in the % decomposition from such solutions.

Finally, by increasing the total specific surface area of the seed, fine precipitated hydrates with a lower mean diameter and a larger specific surface area were synthesized.

Based on the SEM images of the samples of the corresponding properties magnified 50.000 times, a clear difference can be seen. The samples that have a smaller specific surface area and a larger average particle size have larger crystals. The increase in specific surface area clearly shows that the crystals are shrinking and becoming more irregular.

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