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ZINC REMOVAL FROM BAYER LIQUOR BY USING ALUMINIUM HYDROXIDE WITH SPECIFIC STRUCTURAL PROPERTIES AS CRYSTALLIZATION AGENT

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Abstract

The presence of Zn compounds in alumina reduces the current efficiency during electrolysis and quality of obtained metal. The known methods for Zn compounds removal that involves the use of different chemical agents (e.g. sulphide) are uneconomical and not environmentally friendly. In this research, aluminium-hydroxide with specific structural properties (AHSSP) was used as a crystallization agent during purification of Bayer liquor. The specific structural properties of the used aluminium-hydroxide are related with a small particle size (<8μm), small specific surface area (≈3 m^2/g), and large pore diameter (≈1μm). Mechanism of Zn removal is based on crystallization phenomenon of aluminium-hydroxide from Bayer liquor where the AHSSP presents crystallization agent (seed). The crystallization process is conducted to a certain Na_2O/Al_2O_3 ratio, which corresponds to a satisfactory aluminium concentration in Bayer liquor. The crystallization process was conducted in laboratory crystallization vessels (2 dm^3) equipped with a heater and stirrer. The crystallization temperature was 50±1°C and the concentration of aluminium-hydroxide as crystallization agent (seed) was 15, 20 and 30g/l. The concentration of Al, Na, and Zn in Bayer liquor and solid crystallization product (aluminium hydroxide as seed and aluminium hydroxide from Bayer liquor) was analysed by using ICP-OES (Specto Genesis) and AAS (Shimadzu AA7000). The particle size of the obtained solid crystallization product was analysed by Cilas 1090, laser particle size analyser. The specific surface area was determined by using Gemini VII, whereas the pore structure was analysed by using Mercury intrusion porosimetry (Carlo Erba Porosimeter 2000). The obtained results show that the per cent of removed Zn compounds was above 80 for 2h, whereas Al concentration decreased slightly less than 20% for the same time. Structural analysis is shown, that particle size and pore diameter were increased, whereas the specific surface area was decreased. For this reason, the possibility of using the aluminium-hydroxide as a product of this process, without structural modification, is maximally two times.

Keywords: Zn-compounds, crystallization, alumina, and structural properties.

INTRODUCTION

Some bauxite contains a very high concentration of zinc compounds, such as sphalerite (ZnS), gahnite ($ZnAl_2O_4$), and some zinc compounds in which structure Fe, Pb, Cu, and Mn compounds are incorporated (zincophorite ($Al(Zn_xMn_{1-x})O_2(OH)_2$), woodruffite ($2(Zn, Mn)\cdot 5MnO_2\cdot 4H_2O$), in structure of chalcopyrite) (Bánvölgyi, 2017), (Bird et al., 2016). The zinc concentration in bauxite varies depending on the bauxite type (krast and lateritic) and location of exploitation. Bauxite from the sites in Bosnia and Herzegovina consists about 0.012-0.025% ZnO. The ZnO content in the bauxite from Montenegro region, Podgorica and Nikšić, is around 0.035% and 0.0436%,

respectively. In the other worldwide sites, the ZnO content is substantial in the bauxite from Hungary (0.0146%), Northern Ural (0.024%), Brazil (0.0083%), Jamaica (0.02-0.1%), and Guinea (0.0034%) (Bánvölgyi, 2017). During alumina production by Bayer, alkali fusion process, Zn as the impurity at higher digestion temperature (above 150°C) is extracted and becomes part of the Bayer liquor (sodium-aluminate solution) and finally the part of the final product (alumina). According to US Patent 3469935A, the maximal concentration of ZnO in alumina is strictly specified at 0.017% (Hrishikesan, 1969). The presence of Zn in higher concentration can cause a serious problem during the electrolysis process. Sterten et al. (1998) investigated the individual influence of impurities in alumina on the electrolysis process, where it was shown that impurities such as Fe, P, Si, Zn, Ti, and Ga influence on decreasing of current efficiency during electrolysis. The noted decreasing was within the range of 0.1 to 0.7% per 0.01 wt % of impurity cations present in the electrolyte. Also, during electrolysis such impurities, including Zn, can be incorporated in aluminium structure, which leads to lower in quality of the obtained metal. In order to remove these impurities, there are various methods, such as precipitation with alkaline metal sulphide (e.g. Na_2S) (Walter, 1959), filtration through a bed of particles of a granular substance containing Fe_2O_3 (Paul, 1983) and treatment of Bayer liquor with polymeric quaternary ammonium salts (Strominger, 1994). However, the main disadvantages of these processes are non-economy and toxicity. In some industries, these processes are abandoned or rarely used. In this paper, the controlled crystallization process in which aluminium-hydroxide with specific structural properties (AHSSP) was used. The specific properties of this aluminium-hydroxide are reflected in its low-grain size (<8μm) and low specific surface area (≈3 m^2/g). The basic task of such aluminium-hydroxide is to encourage the process of crystallization of aluminium hydroxide from the Bayer liquor, where the crystallization process is carried out to certain Na_2O/Al_2O_3 ratio. During crystallization process, a part of aluminium hydroxide from Bayer liquor together with impurities, such as Zn, passes into solid aluminium hydroxide, while the Bayer liquor, on the one hand, has a lower aluminium content, more importantly, a lower content of impurities.

MATERIAL AND METHODS OF WORK

Bayer liquor and AHSSP were taken from the production process of the Alumina factory in Zvornik, Bosnia and Herzegovina. The crystallization process was conducted in 2 dm^3 laboratory glass equipped with the magnetic stirrer at 50±1°C with three different AHSSP concentrations: 15, 20, and 30 g dm^{-3}. All experiments were conducted as follows: Bayer liquor is heated at crystallization temperature, the AHSSP was measured and added in Bayer liquor after the temperature has been reached, the process was followed by measuring Na_2O/Al_2O_3 ratio and interrupted at the moment when the Na_2O/Al_2O_3 ratio was 2.0±0.1. After crystallization, Bayer liquor was filtered and obtained precipitate was washed with demineralized water and dried overnight at 105°C. Such precipitant was tested as a crystallization agent in the next crystallization cycle. Na_2O, Al_2O_3, and ZnO concentrations in initial Bayer liquor were 157.3, 173.4, and 0.0835 g/l, respectively.

The concentraion of Na_2O and Al_2O_3 in initial Bayer liquor and Bayer liquor after crystallization was determined by using ICP-OES (Spectro Genesis), whereas ZnO concentration was determined by using atomic absorption spectroscopy (Shimadzu AA7000). The structural and morphological properties of the AHSSP, particle size (Laser Particle Size Analyzer, CIlas 1090), specific surface area (Gemini VII, Micromeritics), average pore diameter, vol.% porosity, pore volume, and bulk density (Mercury Intrusion Porosimetry, Carlo Erba Porosimeter 2000), were analyzed.The samples obtained in experiments with different concentrations of AHSSP are labelled as Xg dm^{-3} AHSSP (X=15, 20, and 30 g dm^{-3}).

RESULTS AND DISCUSSION

The concentration profiles of aluminium (Al_2O_3) and zinc (ZnO) are shown in Figure 1 a and b. The obtained results show that concentrations of Al_2O_3 and ZnO decrease during crystallization. In the system with AHSSP concentration of 15 g dm^{-3}, the crystallization lasted slightly less than 4h, whereby the Al_2O_3 and ZnO concentrations decreased approximately 20% and 80%, respectively. The increase in AHSSP concentration reduces crystallization time, so that in systems with AHSSP concentration 20 and 30 g dm^{-3}, the crystallization lasted around 2h, whereas the reduction in concentration of Al_2O_3 and ZnO in Bayer liquor was the same as in the case with the concentration AHSSP of 15 g dm^{-3}.

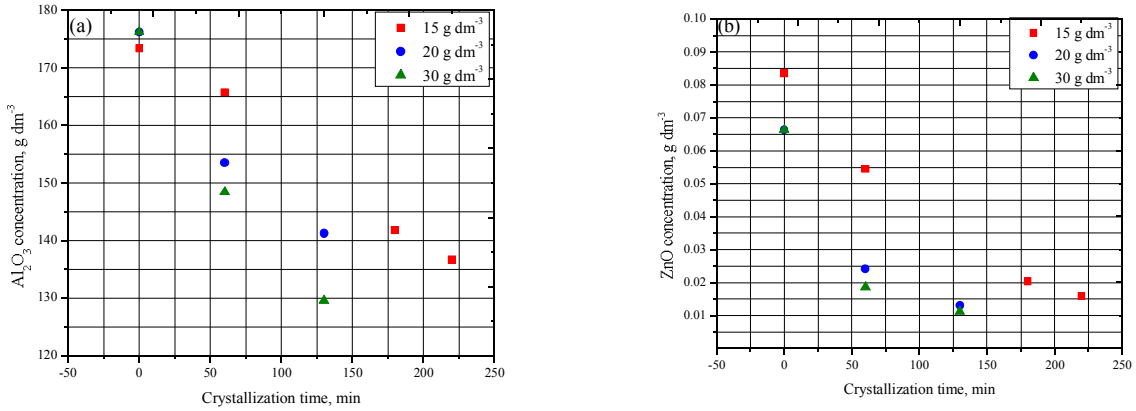

Figure 1. The concentration of a) Al_2O_3 and b) ZnO during the crystallization process at different concentrations of the AHSSP

The obtained results can be explained by the crystallization nucleation theory. At higher AHSSP concentrations, a greater number of crystallization centres exist in system reducing the induction period, and therefore the crystallization time.
The structural properties of AHSSP are shown in Table 1.

Table 1. Structural properties of the initial AHSSP and AHSSP after crystallization process

Sample	[a]d_p (μm)	[b]SSA (m^2 g^{-1})	[c]$D_{p,average}$ (μm)	[d]V_p (cm^3 g^{-1})	[e]BD (g cm^{-3})	[f]P (vol:%)
AHSSP	1.50	3.49	0.69	0.66	0.91	59.9
15 g dm^{-3} AHSSP	10.32	1.32	n.d.	n.d.	n.d.	n.d.
20 g dm^{-3} AHSSP	7.62	1.58	4.1	1.00	0.69	68.6
30 g dm^{-3} AHSSP	6.01	1.71	3.0	0.91	0.76	69.1

a-mean particle size, b-specific surface area, c-average pore diameter, d-specific pore volume, e-bulk density, f-porosity, n.d.-not defined

The mean particle size rises during crystallization. In the system with lower AHSSP concentration, the number of crystallization centres is also lower, and mean particle size is higher in relation to the system where the AHSSP concentration was higher (20 and 30 g dm^{-3}). Other structural properties are related with previous explanation, specific surface area decrease and from porosimetry results, it can be seen, that during crystallization, the newly formed particle has a larger pore volume and

diameter, whereas the porosity increase from 60 % for initial AHSSP to approximately 70% for AHSSP after crystallization from the system with AHSSP concentration of 30 g dm^{-3}.
The concentration ZnO in the solid crystallization product for concentrations of AHSSP 15, 20, and 30 g dm^{-3} was 0.0202, 0.0211, and 0.0230 %, respectively. The obtained solid product in the first crystallization cycle was tested as a crystallization agent in the second. The concentration of Al_2O_3 and ZnO are shown in Figure 2 a and b.

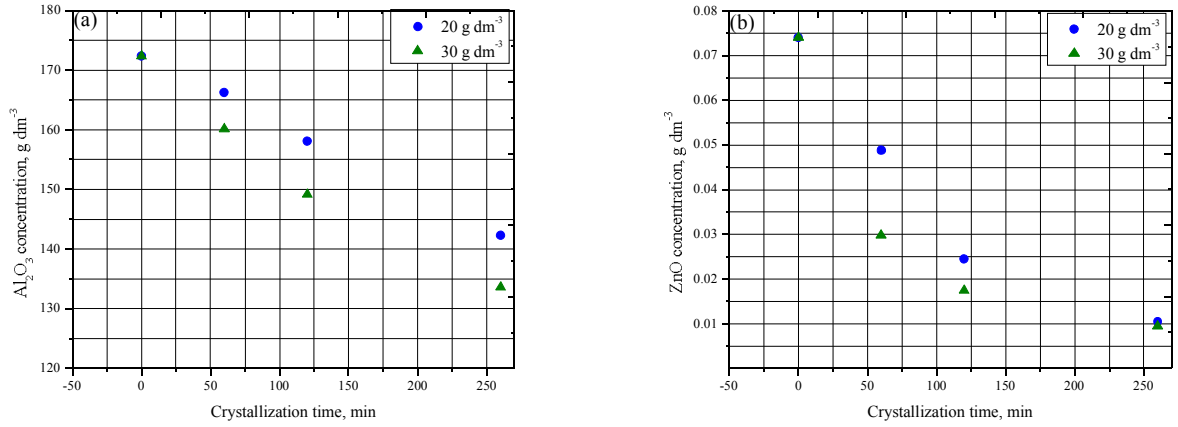

Figure 2. The concentration of a) Al_2O_3 and b) ZnO during the crystallization process at different concentrations of the AHSSP in the second cycle

In the case, AHSSP concentration 20 and 30 g dm^{-3} in the second cycle, the crystallization time was extended for 2.5h. Crystallization process with AHSSP concentration of 15 g dm^{-3} lasted more than 8h, which is much longer than it was in the first cycle. It can be explained by the fact, that at the lower AHSSP concentrations, a larger particle is obtained which in the second cycle leads to an extension of the induction period. Therefore, the AHSSP can be used maximally two times without any modification.

CONCLUSIONS

In order to remove zinc compounds from Bayer liquor, the aluminium hydroxide with specific structural properties (AHSSP) was used as a crystallization agent. The crystallization process was conducted with three different AHSSP concentrations. 15, 20, and 30 g dm^{-3}. The highest zinc removal is achieved at the AHSSP concentration above 15 g dm^{-3} (20 and 30 g dm^{-3}), where the ZnO concentration in Bayer liquor is reduce from 0.0664 to 0.0113 g dm^{-3}. The used crystallization agent during the process has changed structural properties (particle size, specific surface area, pore volume, and pore diameter) which contributed to the extension of the crystallization time. Therefore, the AHSSP and the precipitant obtained in the first cycle (AHSSP with different structural properties) can be used maximally two times without any modification in terms of reduction of mean particle size.

LITERATURE

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