AA21 - The Influence of Process Parameters on Removing Iron, Zinc and Copper Impurities from Synthetic Bayer Liquor

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Abstract

The chemical quality of precipitated aluminum hydroxide, and consequently the final alumina product in the Bayer process directly depends of the level of impurities in a refinery's Bayer liquor. To reduce the concentration of these impurities below the level which affects the quality of final product, impurity removal processes are necessary. Most of these rely on the treatment of Bayer liquor to decrease the level of dissolved impurities, and this study examines impurity removal rates as a function of temperature, alumina trihydrate seed concentration and reaction time. The objective of this study was to identify the optimum process parameters to remove as much iron, zinc and copper from liquor as possible, while minimizing aluminate precipitation. A synthetic Bayer liquor (sodium aluminate solution) was used. Results revealed that with optimized process parameters, it is possible to decrease the starting concentration of iron, zinc and copper in the prepared sodium aluminate solution by up to 100 %. Results showed that even 25 min after seed introduction, concentrations reached 1.12 ppm of zinc, 1.43 ppm of iron and 1.04 ppm of cooper, i.e. almost 90 % removal was achieved. A starting temperature of 40 °C gave zinc and copper concentrations below their detection limit, while 84 % of iron was removed. The best results were obtained with 3 g/L of seed, where the concentration of all three impurities were reduced to below detection limit. The study results indicate that the impurity removal rate is correlated to the precipitation of alumina hydrate from solution, as expressed by the change in molar ratio between caustic (Na_2O) and alumina (Al_2O_3) in the liquor (α_K).

Keywords: Bayer process impurities, sodium aluminate, seed crystals, alumina, alumina hydrate.

1. Introduction

The Bayer process is the most widely used process for alumina and alumina trihydrate production. The alumina produced by this process is most commonly used for the production of aluminum metal, but the Bayer process product can also be used (for example) as a catalyst carrier, filler, abrasive, and as a raw material for the production of many other compounds. There are certain requirements regarding the level of impurities in alumina for all of these applications, since the quality of precipitated aluminum hydroxide, and consequently the final alumina product directly depends of the level of impurities in the Bayer liquor. To reduce the concentration of these impurities below the level which affects the quality of final product, impurity removal processes are necessary.

Leaching (or 'Digestion') is the first stage of the Bayer process. Ground and homogenized bauxite is mixed with a NaOH solution (Bayer liquor) at high temperatures and pressures, whereby selective dissolution of aluminum compounds occurs, and the vast majority of other compounds (i.e. impurities), remain in the solid phase [1,2,3]. Beside aluminium, other undesirable Bauxite elements which are soluble in Bayer liquor under the given conditions, are also extracted into the liquor phase.

Depending on the dominant alumina mineral in the bauxite, the leaching conditions differ. The easiest to leach is gibbsite, followed by boehmite and diaspore, the latter requiring the highest temperatures and pressures, which results in relatively higher processing costs and therefore generally poorer economics than for gibbsitic or boehmitic bauxites [4,5,6,7].

The main reactions occurring during the leaching process are [8]:

$$Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4 \quad (1)$$

$$AlOOH + NaOH + H_2O \rightarrow NaAl(OH)_4 \quad (2)$$

The leaching operation is followed by filtration, which separates the red mud from the aluminate rich Bayer liquor [9, 10, 11].

Industrial Bayer liquors almost always contain impurities that affect its productivity, as well as the quality of hydrate and alumina products for different applications [12, 13]. However, the optimum processes and conditions for economic impurity removal remain a subject without cheap, easy or perfect answers, and an area for further investigation, and the motivation for this study.

2. Experimental

The experimental work was performed using standard glassware, A.R. chemicals, instruments and methods of the research laboratory at "Alumina" d.o.o. Zvornik, Bosnia and Herzegovina.

This study's focus was on removing iron and zinc impurities from synthetic Bayer liquor (sodium aluminate solution), by adding specially prepared alumina trihydrate seed crystals at an optimum ratio [14,15]. Apart from this method, many other ways of removing the nominated impurities from Bayer liquor have been investigated and reported in the open literature. These methods include (for example): removal of Zn and Cu by filtration through a layer of granules containing iron trioxide [16], removal of Zn by addition of ZnS seed in the presence of sulfide ion [17], removal of Fe by filtration through a layer of sand [18].

Removal of iron and zinc from Bayer liquor is achieved in this study by adding specially prepared aluminum hydroxide seed crystals. Chemical analysis of the prepared seed was carried out before the test work. A synthetic Bayer liquor was prepared by dissolving a non-metallurgical alumina trihydrate in a sodium hydroxide solution. The sodium hydroxide solution was prepared by dissolving granular NaOH solid in water. It was empirically determined that 204 g of solid NaOH per liter of demineralized water is needed to dissolve 260 g of non-metallurgical hydrate. The concentration of the resulting solution and the molar caustic to alumina ratio (α_K) are adjusted to the level of Bayer process liquor.

The experiments were performed by monitoring the effects of time, temperature and seed crystal concentration on impurity concentrations:

- The time varied from 15 to 75 min. at constant temperature (50 °C) and seed crystal concentration (5 g/L).

- The temperature was varied between 40 to 75 °C, at constant time (120 min.) and seed crystal concentration 5 g/L.
- The seed crystal concentration varied from 1 to 6 g/L, while other parameters, as in previous cases, remained unchanged (time 120 min, temperature 50 °C).

The experiments were performed in a stirred reactor with a heat exchanger that kept the temperature constant. The first 6 cases were a kinetic study and performed by dividing the reaction mixture into 5 equal parts and after each defined time interval, one of these were taken and analyzed. After 75 minutes, the effect of time was examined. The other 9 analyses were performed individually.

After each simulation, vacuum filtration was performed. The liquid phase was analyzed for impurities and the caustic module (caustic to alumina molar ratio, or 'α_K') was determined to show how much alumina trihydrate the liquor had precipitated during the treatment time.

The solid phase was washed with distilled water until a no hydroxide ions could be detected. After washing, the aluminum hydroxide product precipitated from the sodium aluminate solution was then dried. The dried alumina trihydrate was analyzed for chemical composition, particle size distribution and specific surface area.

3. Results and Discussion

As mentioned earlier, after the completion of the experiment, both the synthetic Bayer liquor and the solid phase were analyzed. It is assumed that the impurity removal mechanism is by adsorption, where the iron and zinc impurities present in the liquor adsorb and remain on the seed crystal. In this way, zinc and iron impurities are removed from the Bayer liquor, making it more suitable for the production of special types of aluminum hydroxide by conventional precipitation.

For each of the 15 treatments, the same aluminum hydroxide seed was used. The Chemical composition of the seed is given in Table 1.

Table 1. Elemental composition of seed.

Elements	Concentration
Si [%]	0.012
Fe [%]	0.009
Na [%]	0.1
Cu [%]	0.003
Zn [%]	0.008
Ca [%]	0.007

3.1 Effect of Time on the Fe, Zn and Cu Removal Process

As stated, for this test, the effect of different time intervals on the Fe, Zn and Cu removal process of the synthetic Bayer liquor i.e. the change of the concentration of Fe, Zn and Cu ions (Figure 1) was monitored at a constant temperature (50 °C) and seed concentration (5 g/L).

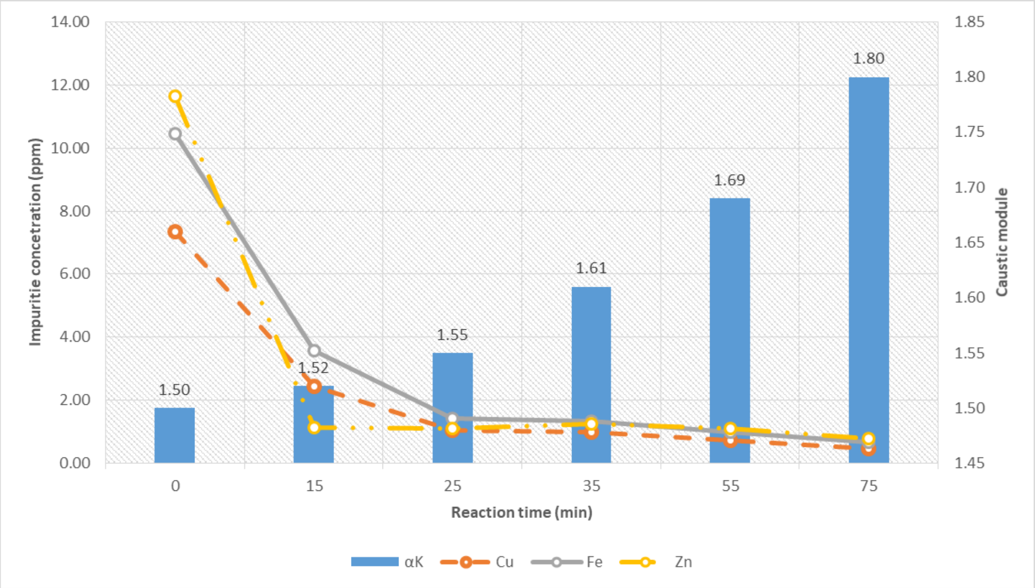

Figure 1. Change in Fe, Zn and Cu concentration in solution vs. time.

The results showed a significant drop in the concentration of iron, zinc and copper, even after 15 minutes, where the concentration of zinc dropped by 90.2 %, iron by 65.8 % and copper by 68.2 % with slight increase in α_K (1.52). As the treatment time increased under the given conditions, the concentration of all three impurities decreased, so that after 75 minutes the concentration of Cu dropped to 0.48 mg/L, Zn dropped to 0.78 mg/L, and the concentration of Fe reached the value of 0.66 mg/L. Based on the increase in the α_K, some alumina trihydrate had precipitated. At the experiment final time (75 min), all three impurity concentrations decreased: by 93.67 % for iron, 93.2 % for zinc and 93.47 % for copper, but with 20 % precipitation yield. From this point of view, the yield is a loss in precipitation productivity in the downstream precipitation circuit.

The results show that the longer reaction time gives better results for impurity removal but results in bigger alumina losses. So main focus was to reach the best possible impurity removal with the smallest possible change in α_K. The greatest drop in zinc concentration was after 15 min, while for iron and copper a little longer reaction time was needed. At a reaction time of 25 min the concentration of zinc, iron and copper dropped to an acceptable level, while precipitation yield was 3.33 % (α_K increased to 1.55), which means lower alumina losses while still achieving acceptable impurity removal. From Figure 1, these changes in concentration can be seen more clearly.

The analyses of the solids from the test are shown with their reaction time in Table 2. The percentage of Fe, Zn and Cu increases compared to the starting seed, which indicates adsorption (or other mechanism for inclusion in the solids) of iron and zinc on the surface of the seed crystals.

Table 2. Results of solid phase analysis after Fe, Zn, Cu removal process vs. time effect.

Time, [min]	α_K	Cu, [%]	Fe, [%]	Zn, [%]
no treatment	1.50	0.003	0.009	0.008
15	1.52	0.027	0.029	0.030
25	1.55	0.026	0.031	0.028
35	1.61	0.013	0.015	0.019
55	1.69	0.017	0.021	0.027
75	1.80	0.012	0.014	0.019

The largest increase in the concentration of these impurities was after 15 minutes, corresponding to the largest concentration drop in the solution (Figure 2).

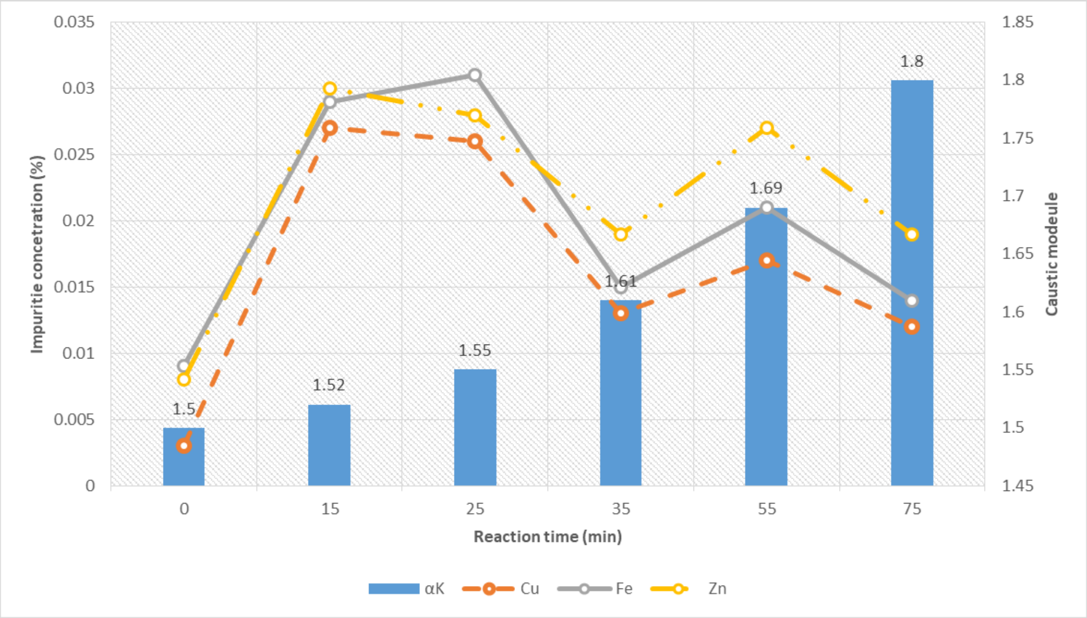

Figure 2. Change in Fe, Zn and Cu concentration in solid phase vs. time.

After 15 min reaction time there was a sharp increase in the concentration of impurities in the solid phase, and with further increase of time, the impurity concentrations started to decrease. This observation can be explained by the start of alumina trihydrate precipitation. The newly precipitated alumina trihydrate increases the total mass of aluminum trihydrate in the solid phase, and thus reduced the concentration of impurities that are adsorbed on the surface of the crystals.

3.2 Effect of Temperature on the Fe, Zn and Cu Removal Process

As in the previous case, one of process parameters was varied. This time with a fixed concentration of added seed (5 g/L) and with constant time of 120 min., the effect of temperature on impurity removal was examined. The results (see Figure 3) show that removal is very efficient at lower temperatures, but with increasing temperature, removal efficiency decreases. As can be seen from the results, the removal of impurities is correlated with precipitation of alumina trihydrate. With a fixed reaction time of 120 min and temperature of 40 °C, there is already significant increase in α_K, indicating fast precipitation was fast, giving the precipitation yield of 35.7 %. At these conditions, a complete removal of zinc and copper was obtained, while iron removal was 84.6 %.

Since the rate of precipitation was high with these process conditions, it is assumed that the nucleation process dominated the crystallization of the alumina trihydrate. It is further assumed that newly formed nuclei, together with added seed, serve as adsorption sites for the impurities from solution. Since the α_K reaches 2.05 and precipitation yield is 35.7 %, a lot of new nuclei are formed under these conditions providing a large total surface area for adsorption.

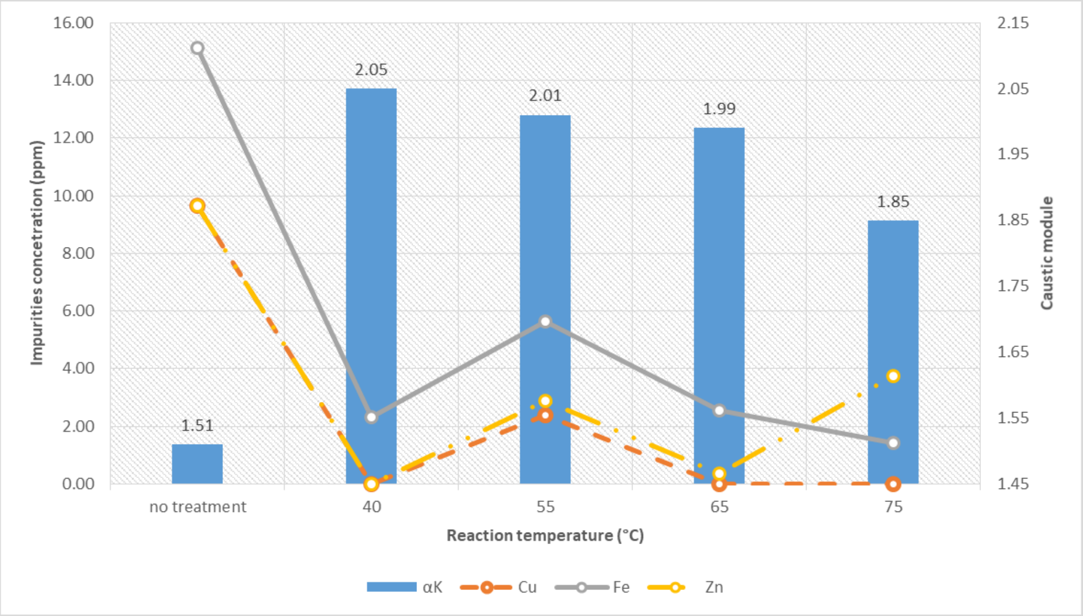

Figure 3. Change in Fe, Zn and Cu concentration in solution vs. temperature.

With further increases in temperature, the removal efficiency slightly decreased. This came with a slightly lower α_K at the end of the reaction. With the increase in temperature, the precipitation rate decreased (due to lower aluminate supersaturating) resulting in lower precipitation yield and lower total surface area available for the adsorption of impurities. Even if a little lower, impurity removal efficiency was still good, but these process conditions resulted in bigger losses of alumina trihydrate, as indicated by the precipitation yield at the end of reaction.

Table 3. Results of solid phase analysis after Fe, Zn, Cu removal process vs. temperature.

Temperature (°C)	α_K	Cu, (%)	Fe, (%)	Zn, (%)
no treatment	1.51	0.003	0.009	0.008
40	2.05	0.013	0.016	0.019
55	2.01	0.010	0.012	0.014
65	1.99	0.011	0.014	0.016
75	1.85	0.013	0.016	0.014

Based on the results in Table 3, it can be concluded that the concentration of impurities in the solid phase increases, as in the case of reaction time. Compared with the temperature response, the impurity concentration increase with time is not so sharp, due to the higher precipitation yield (higher increase in α_K), the increased alumina trihydrate precipitated lowers the percentage of impurities in the seed, as shown in Figure 4.

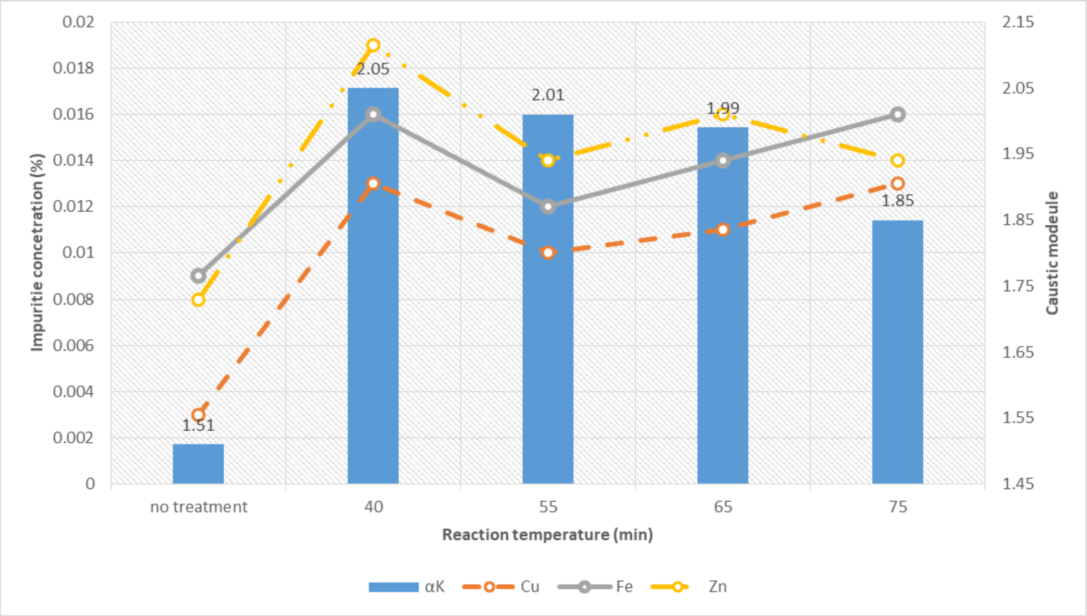

Figure 4. Change in Fe, Zn and Cu concentration in solid phase vs. temperature.

3.3 Seed Concentration Effect on the Fe, Zn and Cu Removal Process

Finally, the influence of the seed charge (the concentration of alumina trihydrate added) was examined. In this case, the seed amount was changed at a fixed time (120 min) and temperature (50 °C). Figure 5 shows the results of the experiment.

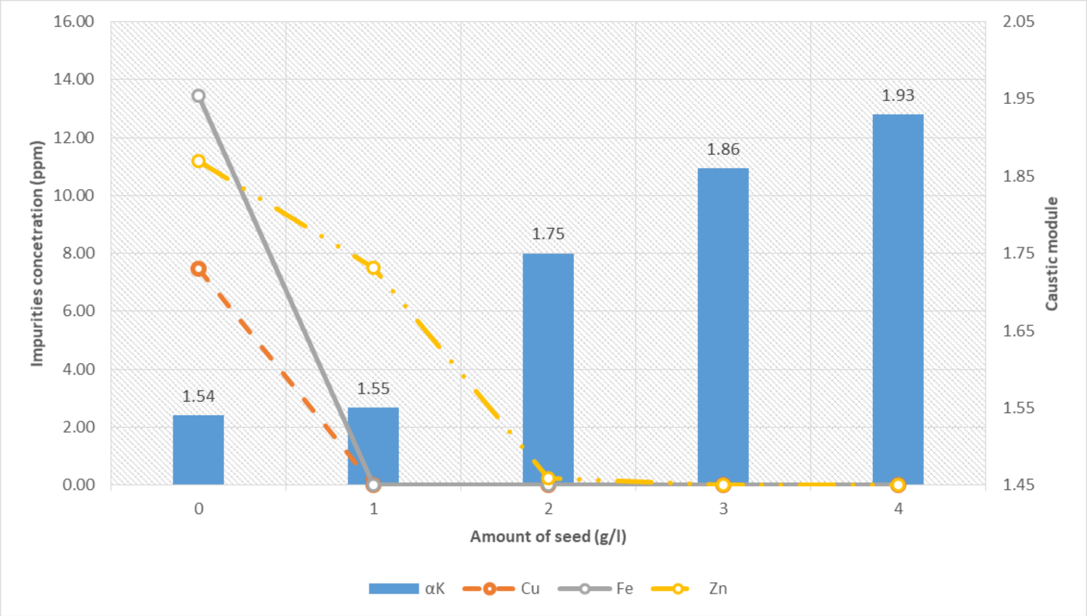

Figure 5. Change in Fe, Zn and Cu concentration in solution vs. seed concentration.

The results, shown in Figure 5, indicate that even with a small amount (1 g/l) of seed at optimum process conditions, 100 % removal of iron and copper is possible. In the case of zinc, it is a 32.8 % decrease in concentration. It is interesting to note that after 2 h with this concentration of seed and at 50 °C, there was almost no precipitation, indicated by an almost negligible change in the αK. Precipitation yield in this case was only 0.6 % for 2h, which indicates a very low precipitation rate compared with 3.33 % for only 25 min reaction time but at a higher seed concentration (5 g/L), where the removal of zinc was more than 90 %.

In the case where 3 g/L of seed is added at these process conditions, 100 % zinc removal also results, but with an increased α_K, and precipitation yield of 20.77 %. With further seed charge increases, complete removal is repeated, but with even higher α_K and precipitation yield (1.93 and 25.3 %). This indicates that a higher seed charge increases the precipitation rate, which is of course, consistent with what is understood about precipitation of alumina trihydrate from sodium aluminate solutions. Figure 1 show that the majority of impurity removal occurs in a period with very little precipitation. It is assumed that adequately prepared seed and a longer contact time are required for the adsorption of iron and copper, while for efficient zinc removal it is necessary for precipitation to occur.

Table 4. Results of solid phase analysis after removal process vs. seed concentration.

Seed amount, [g/L]	α_K	Cu, [%]	Fe, [%]	Zn, [%]
no treatment	1.54	0.003	0.009	0.008
1	1.55	0.074	0.096	0.040
2	1.75	0.017	0.021	0.025
3	1.86	0.013	0.016	0.019
4	1.93	0.011	0.014	0.015

Concentrations of all impurities in the solid phase increase sharply, especially iron and copper in the case of 1 g/L seed, while the zinc increase is not so sharp due to lower removal from solution (32.7 %) compared with complete removal of iron and copper (Figure 6).

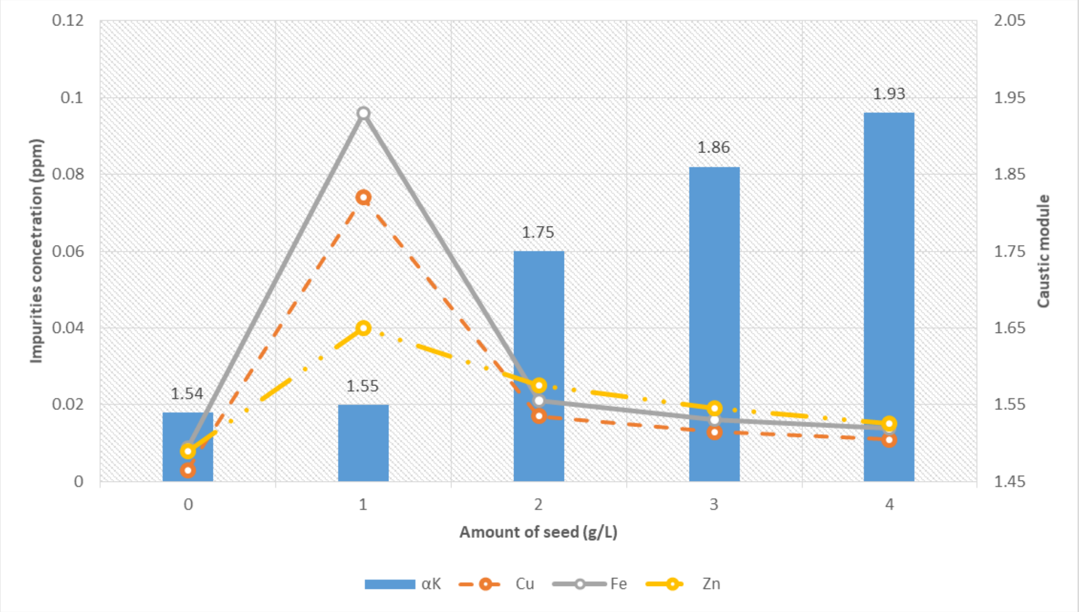

Figure 6. Change in Fe, Zn and Cu concentration in solid phase vs. seed amount.

It is observed that with increasing the seed amount to 2 g/L, the concentration of iron and copper drops significantly and zinc concentration drop is lower because of additional removal of zinc from solution. With further seed increases, concentrations of impurities in the solid phase decreases significantly due to higher yields of alumina trihydrate.

4. Conclusions

When reviewing the scientific and technical literature, it was concluded that the current processes of impurity removal in Bayer liquor are not efficient enough, are too complex and/or economically unacceptable. In this paper, the effect of seed added, under different process conditions and concentrations, to remove iron, zinc and copper from Bayer liquor was investigated.

Based on the results presented here, it can be concluded that:

- Increasing the time of contact between liquor and seed crystals has a positive effect on the removal of iron, zinc and copper liquor impurities.
- Increasing the temperature reduces the impurity removal efficiency from the sodium aluminate solution indirectly because with higher process temperature rate of precipitation is lower and solubility of all impurities is higher. At a temperature of 40 °C, good impurity removal results are achieved.
- The effect of seed crystal concentration is most significant, with 1 g/L it is possible to remove iron and copper completely with negligible increase in α_K, which is most interesting because of the minimised productivity losses and therefore the most positive economics. With further increases in seed concentration it is possible to remove zinc from the solution but with increased alumina losses (indicated by an increase in α_K). Removal of zinc from Bayer liquor is directly correlated with the precipitation of alumina trihydrate.
- It is possible to remove iron, zinc and copper from Bayer liquor with an efficiency of more than 90%, in such a way that the treated solution is still economically usable in the following stages of processing while obtaining different types of aluminum trihydrate

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