AA20 - The Behavior and Removal of Bauxite Zinc in the Bayer Process

Dong-Zhan Han [1,2] and Er-Wei Song [3]
1. Doctor, School of Metallurgy and Environment, Central South University, Changsha, Hunan, China
2. Professor
3. Engineer
Zhengzhou Non-ferrous Metals Research Institute Co. Ltd. of CHALCO, Zhengzhou, Henan, China
Corresponding author: zyy_hdz@rilm.com.cn

Abstract

Bayer liquor impurities are an important factor affecting Al_2O_3 quality. With the grade of Chinese domestic bauxite decreasing, its impurity composition has become more complex, and impurities' negative effects on product quality have become more obvious. High zinc content in alumina products of Guangxi Pingguo Aluminum results from the high zinc in its bauxite. High zinc in metallurgical alumina has a negative impact on the current efficiency of aluminum electrolysis and the properties of aluminum metal and alloys. The occurrence of zinc in bauxite, the behavior of zinc in the Bayer process and its removal methods are summarized, while different removal methods were analyzed, and the future development direction for zinc removal technology in alumina production is discussed.

Keywords: Bauxite bearing-zinc, current efficiency, removal zinc.

1. Introduction

Chemical impurities in metallurgical alumina can have a large effect on aluminum metal quality. With the degrading quality of bauxite in China, higher impurity content and the impact on aluminum quality have become more obvious. The global quality specification for electrolytic aluminum has become increasingly strict, where the impurity content of the highest quality primary aluminum should not exceed 0.015%.

The zinc content in alumina should not exceed 0.01 %, and to reach this value, the zinc content in Bayer liquor must be controlled to below 15 mg/L [1,2]. In China, the content of zinc in Guangxi bauxite is relatively high (0.025 % as ZnO), and consequently ZnO in alumina in this region is relatively high (>0.015 %), which seriously impacts product quality, and the competitiveness of these refineries. Although zinc has some benefits seeded precipitation (such as contributing to the crystal growth rate, and characteristics of the gibbsite crystal), its high concentration in product alumina will affect the current efficiency of aluminum electrolysis, purity of aluminum ingots and metal and alloy material properties. Suss et al [3] points out that an increase of the Zn ion content in the electrolysis bath by 0.01 %reduces current efficiency by 0.13 %, and the material properties of alloys are affected. For example, aluminum profiles with high zinc content are more brittle and have poor ductility.

A large amount of research on the behavior and removal method of zinc in the process of alumina production have been conducted both in China and globally.

2. Occurrence of Zinc in Bauxite

Zinc is one of the secondary mineral elements occurring in bauxite, where the zinc content can reach up to 0.75 % [3]. ZnO contents of some bauxites in China and globally are shown in Table 1. As shown in Table 1, ZnO contents are a little higher in Karst bauxites, such as those from China, Montenegro, Bosnia Herzegovina, and Russia. Lateritic bauxites such as those from Australia, Guinea and Brazil are generally lower in ZnO by up to an order of magnitude lower than karst bauxites. The zinc content in bauxites from different mining areas of the same country can also be different, like that from North Ural and Komi Republic of Russia. Scavnicar [4] analyzed ZnO content in forty-seven bauxite samples from Montenegro, of which a concentration of 0.012-0.025% was found in forty samples, 0.037 % in four samples and 0.05 % in one sample.

Table 1. ZnO content of some bauxites.

Origin	Australia	Guinea	Brazil	China	Jamaica	Montenegro	Bosnia and Herzegovina	Kazakhstan	Russia	
	Weipa	Boke	Trombetas	Pingguo	All deposits	Niksic	Milici	Krasnookyabrskoye	North Ural	Timan
ZnO, %	<0.005	0.0012	0.0067	0.025	0.040	0.035	0.014	0.014	0.019	0.06

Numerous studies of zinc occurrence in bauxites have shown the wide differences between different areas. Bárdossy [5] found ZnS in Hungarian bauxites, in which he reported that the zinc mineral's particle size is 20-30 µm. Feret, See et al [6] found a new mineral bearing manganese and zinc, and from its X-ray diffraction pattern, it was deduced that its structure was like limonite, and the bauxite's zinc content increases with the MnO_2 content. By systematic analysis of 340 samples from different regions, it was concluded that zinc in bauxite is unlikely to replace iron in goethite or hematite. The lithium content measured by ICP was very low. Due to the difference in ion radius, zinc cannot replace lithium or aluminum. Further analysis by X-Ray Diffraction shows that the new mineral containing zinc and manganese was zinc pyrolusite, whose formula is $Al(Zn_xMn_{1-x})O_2(OH)_2$, where X may vary from 0.02 to 0.24.

Suss et al [3] propose that the zinc content in the Nordic and Ural karst bauxites of Russia is related to the existence of oolitic chlorite ($Fe^{2+}\cdot 1.5AlFe^{3+}\cdot 0.2Mg\cdot 0.2Si\cdot 1.1Ag\cdot 0.9O_5\cdot (OH)_2$). Further analysis by Rieteveld-X diffraction, suggested the new mineral bearing zinc and manganese was "zinc hard manganese ore", whose chemical formula is $Al(Zn_x\cdot Mn_{1-x})\cdot O_2\cdot (OH)_2$, in which x can vary between 0.02 and 0.24. Suss et al [3] thought the zinc content in the Nordic and Russian Ural Karst bauxites is as chlorite ($Fe^{2+}\cdot 1.5AlFe^{3+}\cdot 0.2Mg\cdot 0.2Si\cdot 1.1Ag\cdot 0.9O_5\cdot (OH)_2$). Chinese researchers [1] believe that zinc in Pingguo bauxite exists in the form of sphalerite and smithsonite.

3. Behavior of Zinc in the Bayer Process

3.1 Behavior of Zinc Occurring in Bauxite in the Bayer Digestion Process

The behavior of zinc in bauxite in Bayer digestion is related to its occurrence (concentration and mineral phase), and the dissolution rate mainly depends on its mineral occurrence and digestion conditions. Consequently, the dissolution rate of zinc is different for different digestion conditions and different bauxites. The zinc ore $ZnCO_3$ can be fully reacted with caustic liquor at a lower temperature, while the zincblende (ZnS) is very stable and does not react with sodium aluminate liquor below 240 °C [7].

The results of Ostap [8] show that the dissolution of ZnO is low (10-20 %) at low temperature (about 143 °C). He reported that aluminous goethite is dissolved at high temperature with a large amount of lime. When goethite is converted to hematite, zinc can be completely digestion. Under the above conditions, vanadium and chromium can also be dissolved, so the authors believe that iron in the goethite lattice (FeO(OH)) can be replaced not only by aluminum but also by zinc, vanadium and chromium.

E. Papp et al [9] calculated the material balance of zinc in the process of one alumina refinery in Hungary, which showed that about 2/3 of the zinc reported to red mud, and about 1/3 reported to liquor. The study conducted a high-temperature digestion test with Guangxi Pingguo bauxite and found that under high-temperature digestion conditions, about 2/3 of zinc reported to liquor and 1/3 to red mud, which is contrary to the above research results. In summary, the research clearly and consistently relates the dissolution of zinc in the digestion process to its mineral occurrence in the bauxite and the digestion conditions.

Wu [7] calculated the material balance of ZnO in the production process of the Guangxi Pingguo alumina refinery. The zinc dissolved from Pingguo bauxite is about 75 % of the total, while from the Guizhou Aluminium ore, it is less than 40 %. It is believed that the zinc dissolved is mainly affected by the temperature and the caustic concentration in the digestion liquor. Guizhou aluminum's digestion temperature is 240 °C (lower than Pingguo's 255 °C), while the caustic concentration is also lower than Pingguo's.

Perczel and Miklós [10] conducted a digestion test with one kind of bauxite from Hungarian. It was found that about 50% of the zinc in the bauxite is dissolved in liquor at 180-200 °C.

A number of studies on the species formed during zinc dissolution in Bayer liquor have been reported. A study from the former Soviet Union [11], showed that during the digestion process, zinc-bearing minerals reacted with the caustic liquor, and zinc entered the Bayer liquor as sodium zincate, and $Zn(OH)_4^{2-}$, in a similar structure as $Al(OH)_4^-$, and can be aggregated [8]. Verghese [12] made similar conclusions. The zinc minerals in bauxite were partially dissolved as sodium zincate during the digestion process, and a variable amount of zinc entered the aluminum hydroxide product during the precipitation process. P.J. The [13] proposed that zinc exists in the form of ZnO_2^{2-} or $Zn(OH)_4^{2-}$ in Bayer liquor. Based on research and practical experience of silica and alumina in Bayer liquors, the authors believe that the existence of the zinc in a fine colloidal form, due to the presence of aluminate and carbonate ions in refinery liquor. Suss [3] and other studies confirmed that zinc in sodium aluminate solution exists in the form of $Zn(OH)_4^{2-}$, at least in high concentration solutions.

3.2 Behavior of Zinc in the Bayer Precipitation Circuit

Zinc and aluminum have similar chemical properties owing to their positions in the periodic table. Based on their similar chemistries, sodium zincate and sodium aluminate have some common behaviors in the Bayer process. When sodium aluminate is precipitated as gibbsite, zinc is co-precipitated, contaminating the gibbsite product.

Bujdosó [14] reported that all of the zinc in the pregnant liquor was precipitated during seeded gibbsite precipitation. Teas and Kotte [15] believed that 90 % of the ZnO in the pregnant liquor entered the gibbsite product during the precipitation process.

Романов. Л.Г, et al [16, 17] studied the effects of zinc on precipitation from sodium aluminate solutions and the particle size of aluminum hydroxide formed. The results showed that the effect of 10 g/L ZnO on a sodium aluminate solution is not obvious. A precipitation test, comparing a pure sodium aluminate solution with a sodium aluminate solution having a ZnO concentration of 5.3 g/L, showed that the gibbsite precipitated from the zinc-containing solution had a coarser particle size. Since the ZnO concentration in the industrial Bayer liquors are much lower than that in the above test, it can be considered that zinc does not significantly affect the precipitation yield from sodium aluminate solutions (Bayer liquors) or the product particle size.

Based on the determination of ZnO concentrations, Wu [7] calculated the material balance in a Bayer refinery process. The results showed that the precipitation of ZnO from pregnant liquor in the precipitation process was about 36 %, and the author concluded that the amount precipitated has little relation to precipitation conditions, apart from a higher silicon content in the pregnant liquor lowering the amount of ZnO precipitated.

The author examined the effect of caustic concentration on the precipitation of zinc in the precipitation process of Pingguo alumina refinery. The results show that as the caustic concentration decreases, the yield of zinc increases. It is believed that the yield of zinc in the precipitation process is related to liquor caustic concentrations and precipitation conditions. The alkali concentration of Bayer liquors in monohydrate or gibbsite refineries outside China is lower than in China, and the precipitation yield of zinc is high in the precipitation circuit; while Chinese refineries have higher caustic concentrations, and the precipitation yield of zinc is lower. Precipitation circuits are also different.

4. Processes to Reduce ZnO in the Bayer Process

Zinc reduction processes in alumina production can be classified as chemical or physical (adsorption) methods. Chemical zinc reduction has been studied more than physical processes. The principle of chemical zinc removal is to add some form of sulfur to the process to remove insoluble compounds or complexes, while physical zinc removal relies on zinc adsorption to suitably adsorbent surfaces.

4.1 Chemical Methods

4.1.1 Inorganic Zinc Removal Method

Inorganic zinc removal methods generally utilise sodium sulfide and/or elemental sulfur. The principle is based on the reaction between S^{2-} and Zn^{2+} to form insoluble ZnS, whose solubility product constant is only 2×10^{-24}, and is stable below 240 °C.

Adams [18] suggests that adding sodium sulfide to Bayer liquor can reduce zinc content. Elemental sulfur was firstly added to the bauxite digestion slurry. Only 38 % of S was converted into sodium sulfide at 150 °C, the zinc removal was low, and liquor was contaminated with S and SO_4 ions. Theoretically, zinc removal can be achieved by adding sodium sulfide after the digestion stage and before any precipitation. However, industrial tests have found that adding sodium sulfide after settling is more effective than adding it before. The reason may be that the residual ore in the slurry before settling is not conducive to the precipitation of zinc sulfide.

The author tried to add sodium sulfide directly to the settler to remove zinc, but the results were not ideal. The reason may be that the oxides in the bauxite residue adsorb sodium sulfide. Hrishikesan [19] holds a different opinion on this and believes that adding sodium sulfide to the digestion slurry before sedimentation works well. He proposed that the reaction of sodium sulfide with zinc produces colloidal aggregates of ZnS, rather than the precipitation of ZnS. X-ray diffraction shows that the precipitated ZnS contains many small (colloidal) crystallites, and red mud acts as an absorbent for these small crystallites.

P. J. The [13] pointed out that zinc is amphoteric. Zinc exists in the form of Zn^{2+}, ZnO_2^- (or Zn $(OH)_4^-$) in sodium aluminate solutions, with the latter being the most common. The presence of aluminate and hydroxide ions may lead to the formation of zinc oxide and hydroxide colloids. Other ions in the Bayer liquor may also react with S^{2-}, so the reaction of Zn^{2+} and S^{2-} is not as the simple stoichiometry would indicate, and sodium sulfide usually needs to be added in excess. However, the excess sodium sulfide is oxidized, causing sodium sulfate to quickly accumulate in the liquor, in time reaching a high concentration, resulting in lower precipitation yield and smaller product size. The literature [14,15] points out that a higher sodium sulfide concentration in the solution would lead to a higher iron content in aluminum hydroxide product, due to the formation of $Na_2[FeS_2(OH)_2]\cdot 2H_2O$ which has a high solubility. When 0.6 g/L of sodium sulfide is added, the zinc content in liquor can be reduced to 0.002 g/L. Mixing part of the liquor treated with sodium sulfide and untreated liquor will reduce the zinc content to the usual target, and save sodium sulfide.

Hrishikesan [20] suggested that using red mud as a filter medium to clarify Bayer liquor can reduce the zinc content from 0.024 g/kg to 0.006 g/kg, and the required residence time is short. The study also found that the sodium salts (mainly sulfate, carbonate, and aluminate) discharged from filtration of evaporated liquor can be used as a zinc removal agent after high temperature treatment to remove carbon, with zinc removal better than for pure sodium sulfide. The use of 0.18 g/kg sodium sulfide can reduce zinc in Jamaican digestion slurry liquor to 0.01 g/kg, and the sodium salt discharged from high temperature carbon reduction and evaporation to make sodium sulfide with the same concentration can reduce zinc in the slurry to 0.0006 g/kg.

Byrd and Vance reported adding zinc sulfide as seed with sodium sulfide to Bayer liquor to remove zinc effectively [21]. Although this method provides good zinc removal, it consumes a large amount of raw materials, and the cost is high. The amount of zinc sulfide prepared in [22] was only 1/10 of that in the literature, but the specific surface area of zinc sulfide was large and the activity was good.

Chinese researchers [22] also carried out experimental studies on the removal of zinc from Bayer liquor using ZnS seed. The results show that zinc can be removed from Bayer liquor to below 15 mg/L (which meets the national standard) at the reaction temperature of 60 °C, reaction time of 90 min, sodium sulfide concentration of 0.4 g/L, and ZnS seed addition of 40 mg/L.

Although the addition of sodium sulfide is a simple and effective method for zinc removal, in real operations it is necessary to add an excess of sodium sulfide to achieve good results, due to the zinc concentration in liquor as Zn^{2+} being very small. Excess sulfur ions will accumulate cyclically in the process, which will cause a series of negative effects on alumina production, such as equipment corrosion, increased caustic consumption, decreased precipitation yield, and in some cases, severe scaling.

4.1.2 High-sulfur Bauxite Removal Method

The principle of removing zinc with high-sulfur bauxite is that if during the digestion process, high-sulfur bauxite containing pyrite is added, pyrite will react with the caustic at high temperature, with a large amount of sulfur dissolving, mainly in the S^{2-} state, resulting in the main reaction as below [23]:

$$30NaOH + 8FeS_2 = 4Fe_2O_3 + 14Na_2S + Na_2S_2O_3 + 15H_2O \tag{1}$$

S^{2-} will react with the zinc in the liquor to precipitate ZnS, which will be absorbed by the red mud and removed along with it.

Chinese researchers [24] carried out a bauxite digestion / zinc removal test by increasing the high sulphur ore in the feed. The results show that the presence of sulfur in the bauxite affects zinc removal. Henan high-sulfur ore with pyrite as the main form of sulfur, has a good zinc removal effect, while Guizhou high-sulfur ore where sulfate is the main sulfur compound, is not effective. When Henan high-sulfur ore accounts for between 10% and 20% (mixed with low S ore), the zinc removal was the best. At this time, the zinc content in the digestion liquor can be reduced to less than 0.015 g/L, which not only meets the production specification, but also reduces the high divalent sulfur input into process liquor. Adding high-sulfur bauxite to the digestion feed has no effect on the extraction of alumina (digestion efficiency).

Adding high-sulfur bauxite to remove zinc is effective, and the process is operationally simple, without requiring additional equipment or processes. This method can not only effectively consume high-sulfur bauxite (otherwise difficult to process), but also remove zinc from liquor without additional removal costs and is therefore an interesting zinc removal option.

However, in actual operations, although the amount of high-sulfur bauxite is relatively small, sulfur will still accumulate in the Bayer process liquor, which will result in negative consequences such as equipment corrosion, alkali consumption, and even the generation of $Na_2[FeS_2(OH)_2]\bullet 2H_2O$, which will result in a high iron content in product aluminum hydroxide. The divalent sulfur will also eventually be oxidized to sodium sulfate, which accumulates in the liquor, causing scaling when the sodium sulfate concentration exceeds 8 g/L [25]. As the sodium sulfate concentration increases, the concentration of iron in liquor will also increase, affecting the product quality [26]. For this reason, in refinery operations where high-sulfur ores containing pyrite are added, the amount added must be strictly controlled.

4.1.3 Organic Method

Organic zinc removal is achieved using the organic sulfur reagent such as dithiocarbamate. The principle is to use the large sulfur atom radius, which is negatively charged, such as in dithiocarbamate, and easily polarized and deformed to generate a negative electric field. It can capture cations and bond with them to form insoluble amino dithioformate, by which heavy metal ions are removed as a chemically stable precipitate. Malito [27] studied the removal of zinc from sodium aluminate solutions using organic reagents. The results showed that the several thiocarbamates screened can effectively remove zinc from strong alkali systems, but the molecular weight should not be too high (less than 5000 Daltons). The effect of non-polymeric compounds was obvious, with additions of 0.05 to 1.0 g/L, reaction times of more than 45 minutes. The removal from pregnant liquor was better than from digestion slurries.

Dithiocarbamate is an organic salt, with a small molecular weight, and the complex formed also has a small precipitation yield, a long precipitation time, and is not easy to separate. And while removing zinc, the continuous accumulation of excess organic carbon compounds will adversely affect alumina production, increasing liquor viscosity, reducing the red mud sedimentation rate, accelerating equipment scaling, and degrading the production environment [28]. The development of an efficient, low-cost and environmentally friendly organic zinc removal agent that can efficiently remove zinc, and where the organic complexes formed can be discharged into the red mud leaving very little residual organic carbon, and having little impact on production would be welcomed by the industry.

4.2 Physical Methods

To avoid the disadvantages of Bayer liquor contamination by sodium sulfide due to its excessive addition, Paul [29] reported a method to filter out copper and zinc from Bayer process liquors. This method uses high-silica / high-iron bauxite (A/S = 4.53) as the raw material, in which the ZnO and CuO content are 0.05 and 0.012 % (in alumina products) respectively. The overflow from settling digestion slurry after the high-pressure digestion (230 °C) was used as a test stock solution, in which the ZnO and CuO contents were 0.025 g/L and 0.015 g/L, respectively. The raw liquid was passed through a cylindrical sand bed filter containing an Fe_2O_3 filter media. The content of Fe_2O_3 in the sand bed should be at least 10%, preferably 40 % to 100 %, the particle size of Fe_2O_3 is 100 to 400 µm, and the thickness of Fe_2O_3 sand bed is at least 38 cm. In addition to Fe_2O_3, the sand bed contains SiO_2, TiO_2, Al_2O_3 and other components. The results show that the zinc removal increases with the height of the sand bed and decreases with the volume of liquor passing through the bed. The stock liquor was passed through the 38.1 cm and 69.1 cm sand beds, and the ZnO content of the alumina product decreased from 0.05 % to 0.033 % and 0.012 % respectively. At the same sand bed height, when the sand bed is coated with a layer of saturated zinc sulfide, the ZnO content in the alumina product can be reduced to 0.006 %. Rinsing the filter bed with 1.0 N hydrochloric acid or dilute sulfuric acid 5 times at room temperature made the sand bed reusable.

The physical (adsorption) method provides good removal, and avoids the adverse effects of the inorganic and organic chemical processes. Unfortunately, the filter layer needs to be periodically cleaned and replaced, so the operation is complicated, the additional operating cost is high, and it is difficult to industrialize.

5. Conclusions

Excessive zinc in alumina products has become a restriction on the development of alumina refineries using Guangxi bauxite as a raw material. Where this bauxite is used for alumina production, zinc removal has therefore become a difficult and urgent topic. It is recommended that, first of all, the mineral forms in which zinc occurs in high-zinc bauxites and their behavior in the Bayer process should be further studied to allow optimisation of the digestion conditions for these bauxites, to inhibit the dissolution of zinc. The objective would be to have a large proportion of bauxite zinc leaving the process with red mud, reducing that accumulating in the process liquor. The development of an organic, environmentally friendly zinc removal technology is recommended as the future zinc control technology development direction. The technology should not only effectively reduce the zinc content in the product, but also avoid the negative impacts on the production process that other methods presently suffer from.

6. References

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