Recovery of spent pot linings (SPL) from aluminum production: A thermodynamic process analysis

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Abstract

The aluminium smelting process is performed in a molten salt electrolysis cell that basically contains carbon anodes, molten salts as an electrolyte and carbon cathode covered with insulation lines from outside like a pot. After the end-of-life of cathode, the removed parts are called spent pot lining (SPL), which is a mixture of the carbon (first cut) and refractory materials (second cut). The smelters generate approximately 20 - 40 kg SPL per tonnes of produced aluminium. SPL is a hazardous waste due to the high content of toxic cyanides and fluoride salts. The waste management practice of it is limited as well as costly. This study investigates a new recycling route for detoxification and recovery of SPL by a hydrometallurgical approach to develop a sustainable process for the aluminium industry. The suggested process consists of pre-washing, extraction - detoxification, and precipitation - filtration stages. The process for the recovery of SPL is thermodynamically designed for the first cut which is the carbon-rich section by HSC Chemistry 9 software. The results show that fluoride and cyanides are decomposed by reactive extraction to detoxify the SPL using caustic leaching with hydrogen peroxide addition. Although the decompositions of the toxic substances are thermodynamically favorable, the kinetic factors can cause limitations in the process. SPL particles should be effectively liberated during the pretreatment/grinding stage due to the successful penetration of the leaching solution to the toxic components. The extraction reactions mainly generate sodium fluoride and sodium-aluminium-hydroxide. After the extraction, the detoxified carbon is filtered to remove from the leachate, which can be treated via precipitation reactions using calcium hydroxide leading the formation of solid calcium fluorides.

Introduction

Aluminum is one of the main industrial metal together with iron, copper, and zinc. Its production/consumption is in second place after iron/steel products. Primary Al production has been continuously increasing since the beginning of the 20th century, and global production recently reached around 64 million tons in 2018.

Primary metallic Al is produced from bauxite ore by mineral pretreatment followed by molten-salt electrolysis, known as the Hall-Heroult process. The typical components of a Hall-Heroult cell are given in Figure 1[1-4]. In this process, alumina is dissolved in a molten cryolite bath within a carbon-lined pot, which also acts as a cathode material.

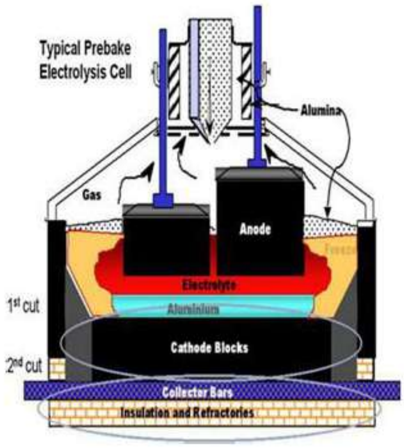

Figure 1. Typical components of a Hall-Heroult cell[3].

Each ton of Al produced in smelters generates approximately between 20 and 30 kg of spent pot lining (SPL), which is a mixture of the carbon lining and the refractory lining. Images of industrial SPL layers are given in Figure 2. It is accepted as hazardous waste because of the high amount of toxic cyanides and fluoride salts content. Considering the current global production amount, the primary Al industry generates roughly 1.28 million tons of SPL in 2018. The current waste management practice of hazardous SPL is landfilling or incineration, which costs aluminum producers on average 200 EUR/ton and 256 million EUR annually on a global level.

Figure 2. Images of spent pot lining of the Al production process [5].

The research presents a novel type of zero waste technology for the recycling of hazardous waste - spent pot linings from aluminum production. The recycled products will be used either in Al production or will be sold to the refractory and/or construction industry. The SPL-CYCLE technology represents a new circular economy business model with the complete elimination of waste landfilling and incineration costs.

Methods

A reaction model was built according to the three main chemical reactions (i) alkaline extraction, (ii) cyanide destruction and (iii) precipitation which are given in Eq. 1, 2 and 3. HSC 9 Chemistry software was used for the thermodynamic modeling of the SPL recovery process.

$Na_3AlF_6 + 4NaOH(a) = 6\ NaF + NaAl(OH)_4$ eq.1

$2NaCN(ia) + 5\ H_2O_2\ (l) = 2\ NaOH + 2CO_2(g) + N_2(g) + 4H_2O$ eq. 2

$2NaF(a) + Ca(OH)2 = CaF_2 + 2\ NaOH(a)$ eq. 3

Results and Discussions

Thermodynamic data, changes of Gibbs free energy, and reaction equilibrium constant of the decomposition of cryolite by alkaline leaching and formation of sodium aluminum hydroxide from cryolite by sodium hydroxide is given in Figure 3a,b. Modeling of the reaction clearly shows that the first cut of the SPL can be treated by an alkaline solution.

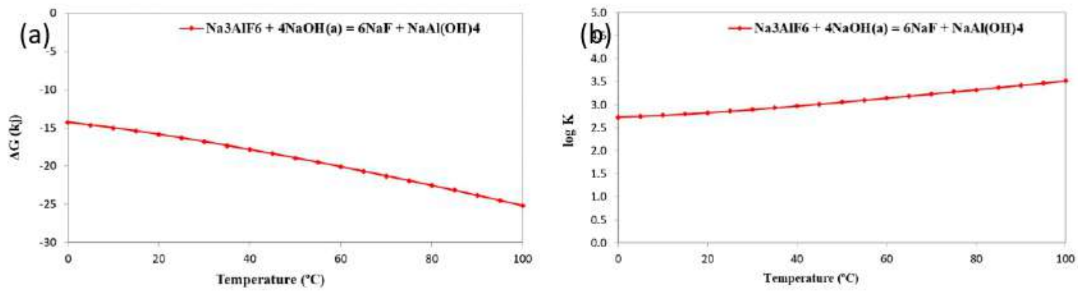

Figure 3. Change of (a) Gibbs standard free energy and (b) reaction equilibrium constant by temperature for the decomposition reaction of cryolite by sodium hydroxide.

The alkaline extraction stage to decompose the cryolite to sodium fluoride and sodium-aluminum hydroxide was investigated as a function of water flow and sodium hydroxide concentration. Equilibrium diagrams of reactants and products are given in Figure 4. The thermodynamic modeling of the process stage shows that a 3 wt% NaOH solution is enough to process the first-cut SPL. Alkaline treatment will decompose the cryolite and formed NaF and $NaAl(OH)_4$ can be treated in the following stages.

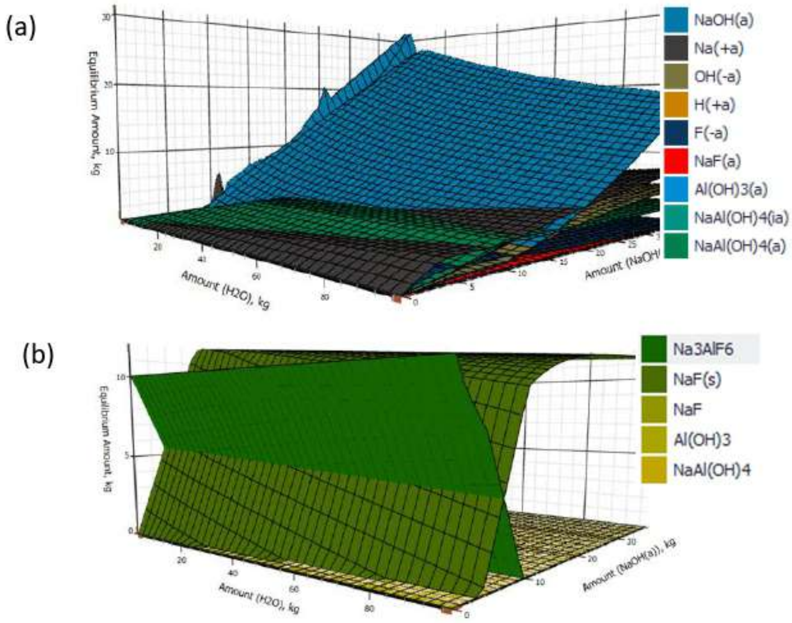

Figure 4. Equilibrium amounts of reactants and products for alkaline extraction of SPL as a function of water flow and NaOH concentration (a) aqueous species and (b) solid species.

The Gibbs free energy change of the sodium cyanide destruction by hydrogen peroxide is given in Figure 5a as a function of temperature from 0 to 100 °C. It is clear that the cyanides can decompose to $CO_{2\ (g)}$, $N_{2(g)}$, and H_2O in the process condition.

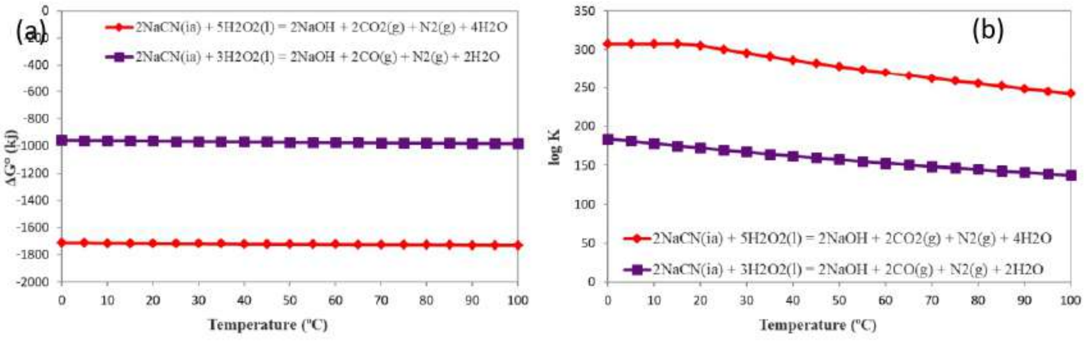

Figure 5. Change of (a) Gibbs standard free energy and (b) reaction equilibrium constant by temperature for the decomposition reaction of sodium cyanide by hydrogen peroxide.

Several side reaction equations were investigated to understand the process chemistry and design a scaled-up process in realistic parameters. Figure 6 shows the Gibbs energy of cryolite decomposition by hydrogen peroxide, which is a possible reaction according to the thermodynamic results.

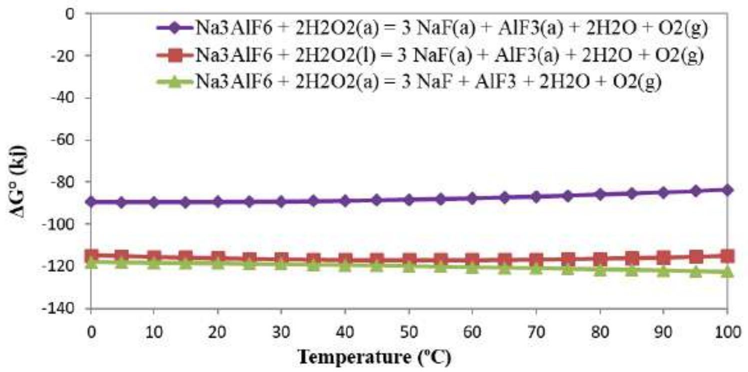

Figure 6. Change of Gibbs standard free energy by temperature for the decomposition reaction of cryolite by hydrogen peroxide.

It is assumed that cyanide distributes the outer and inner porous of the cryolite in the sample. Due to mineral morphology, hydrogen peroxide can be consumed by both cryolite and cyanide. Thus liberation of the particles and alkaline extraction stages are critical for efficient detoxification of the SPL.

Final process water treatment to remove the fluorides from the water by precipitation reactions was studied (Figure 7). The process water after alkaline leaching and cyanide destruction contains a high amount of NaF. The thermodynamic reaction analysis revealed that $Ca(OH)_2$ is a suitable agent to react with NaF to form solid CaF_2. The solid reaction product precipitates and can be easily separated by a thickener and/or filtration unit. After the precipitation reactions, NaOH amount increases in the process water, which can be reused in the alkaline leaching stage.

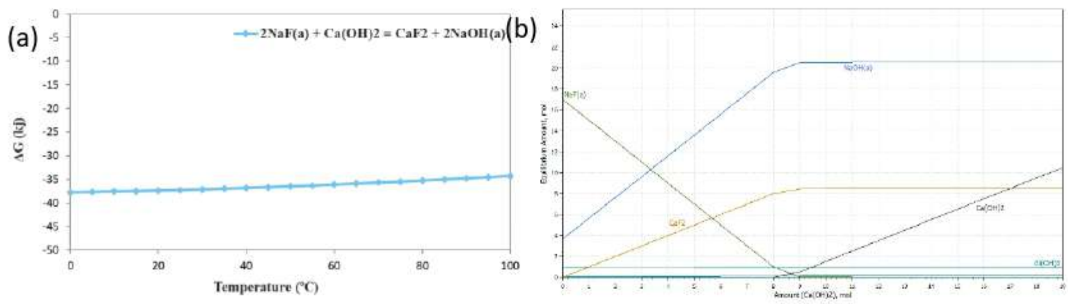

Figure 7. (a) Change of the Gibbs standard free energy by temperature for precipitation of CaF_2 using calcium hydroxide salt, and (b) equilibrium composition of NaF-$Ca(OH)_2$-CaF_2 system by add amount of $Ca(OH)_2$ in simulated content of the waste leaching liquor.

The SPL-CYCLE presents a novel zero-waste technology, for the recycling of SPL from aluminum production, consisting of four main separation processes (preparation, extraction, flotation, and refining) in order to achieve the quality of products needed by end-users. The final products will be used either in aluminum production (recovered carbon and fluoride salts) or will be sold to the refractory industry or the construction industry (recycled refractory residues), with a special focus on the industry in the EU countries and economic partner countries. The developed technology can help them to solve their particular problems, as well as to foster their international competitiveness.

Conclusions

The process for the recovery of SPL is thermodynamically designed for the first cut which is carbon-rich section of the SPL and some hinders for upscaling the technology were revealed considering to kinetic effects.

Liberation of the SPL particles is important during the mineral processing stage to increase the efficiency of the recovery process, as well as optimize the chemical consumption. Considering the other salts in the process water, NaF can precipitate in solid form because of increasing the solubility limit of the salts in the water.

Acknowledgments

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References

1. USGS, Aluminum Statistics and Information Annually Report, 2018, Last Accessed. 2019/08/26, <https://prd-wret.s3-us-west-2.amazonaws.com/assets/palladium/production/s3fs-public/atoms/files/mcs-2019-alumi.pdf>
2. W. Yang, X. Liu, J. Liu, Z. Wang, J. Zhou, and K. Cen, “Thermodynamics analysis of carbothermal-chlorination reduction in aluminum production”, *Applied Thermal Engineering*, **111** 876-883 (2017).
3. G. Holywell, and R. Breault, “An Overview of Useful Methods to Treat, Recover, or Recycle Spent Potlining”, *JOM*, **65** 1441-1451 (2013).
4. G. Liu, D. B. Müller, ”Addressing sustainability in the aluminum industry: a critical review of life cycle assessments”, Journal of Cleaner Production, **35** 108-117 (2012).
5. Randell Environmental Consulting, Spent pot lining project (feasibility of an agreement based approach to clear stockpiles), Final national summary report, October 2016.