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SIMULATING BERYLLIUM ELECTROREFINING WITH AspenPlus©

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ABSTRACT

Beryllium is a lightweight, high strength metal with excellent thermal properties. It is a high cost material that has applications in electronics, the space program, and the defense industry. Beryllium is irreplaceable in several defense applications and therefore the US government maintains a reserve supply of several grades of the metal. However, the current defense industry (the largest metallic beryllium user) use has dwindled to the point that the only metallic beryllium producer in the US, Brush Wellman Inc., continually evaluates the profitability of continued production. The production dilemma has been compounded by health concerns associated with the generation of beryllium fines during production. An electrorefining method, previously developed, shows promise for recycling low purity beryllium scraps and produces a high grade material. Recycling and purification can reduce costs and waste disposal problems and increase the beryllium reserves in the event that Brush Wellman discontinues production. In this paper, we demonstrate how to use a commercially available process simulator for improving a process to electrorefine both scrap and low purity beryllium into a high purity product.

KEYWORDS

Beryllium; Simulation; Electrorefining

1. Introduction

In November 1987, a pilot plant for a process to electrorefine beryllium was implemented at the Rocky Flats, Colorado Plant then operated by Rockwell International. The electrorefining process is a two-step method by which impure materials are ionized at one electrode, in a molten salt bath. The ions diffuse through a conductive medium and are deposited as a nearly pure metal on a second electrode. The first step is the synthesis of beryllium chloride ($BeCl_2$) which serves as a bridge for diffusion through the conductive molten salt. The second step is the electrorefining process which consists of electroplating beryllium from a sacrificial anode, cast from contaminated beryllium machining scraps, onto a cathode through a conductive bath, producing a 99.95% pure beryllium flake at the cathode. This process was modeled in an effort to determine thermodynamically optimal operating conditions for future experimental work. The model was validated using the pilot test results and was scaled for use in the prediction of results for a production scale plant.

In this paper, we demonstrate how a commercially available process simulator was used to enhance and refine a process to electrorefine both scrap and low purity beryllium into a high purity product. The method is thermodynamically complicated because the results depend upon both the phase and the electrochemical nature of beryllium and its associated impurities. We identify optimum temperatures that increase the efficiency and reduce the emissions of an already successful process. Data from these simulations predict that the emissions were kept below the 2 mg/m^3, the OSHA permissible limits, during pilot tests and indicate that this method has the potential to meet the proposed future emission limit of 0.5 to 1 mg/m^3. We modeled each step of the process individually. The simulator used for this task was AspenPlus by AspenTech [1]. The details of the pilot plant operation were obtained from an internal Rockwell report [2]

2. Beryllium Chloride Synthesis

Beryllium chloride must be synthesized so that it can be included in the salt bath required in the electrorefining step. Synthesis was accomplished in the pilot plant by passing chlorine gas over a bed of beryllium chips in a semi-batch reactor. Figure 1 shows the AspenPlus simulation flow sheet for the $BeCl_2$ synthesis step. This is a steady-state simulation of a semi-batch process. In this simulation, hot beryllium (BE-IN) is contacted with chlorine gas (CL2-IN) at room temperature in a reaction vessel (RGIBBS). The reaction continued until chemical equilibrium was reached. The equilibrium composition for the simulation is determined by the minimization of the system Gibbs free energy. Beryllium chloride vapor and unreacted chlorine exit through the EXHAUST steam. Unreacted beryllium exits through the SOLIDS stream.

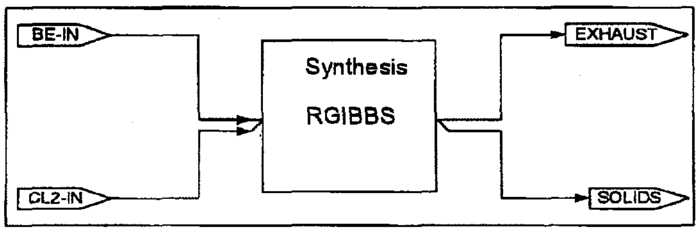

Figure 1. Simulation Flowsheet of the Beryllium Chloride Synthesis Process

In the three pilot plant runs, that each lasted 48 hrs, a 22-pound charge of beryllium was reacted with flowing chlorine feed gas. The gas flow reportedly varied between 2.5-2.7 pounds/hr. The reactor temperature was held at 650°C in each case. In the flow simulation, the beryllium feed to the reactor was held constant at 0.458 pounds/hr, and the reactor was held at 650°C. Three simulations were run using chlorine gas flow rates of 2.5, 2.6, and 2.7 pounds/hr, respectively.

The results from the synthesis simulations are shown in Figure 2. Beryllium chloride generation was predicted to be 2.818, 2.93, and 3.043 pounds/hr for the chlorine feed rates of 2.5, 2.6, and 2.7 pounds/hr, respectively. The simulation results show that on the average, about 72% of the initial beryllium charges were converted to $BeCl_2$ at equilibrium. In the pilot process, where the equilibrium was shifted by a semi-batch reactor, the conversion efficiency was reported to be 82%. The economic considerations and safety trade-offs are still being considered.

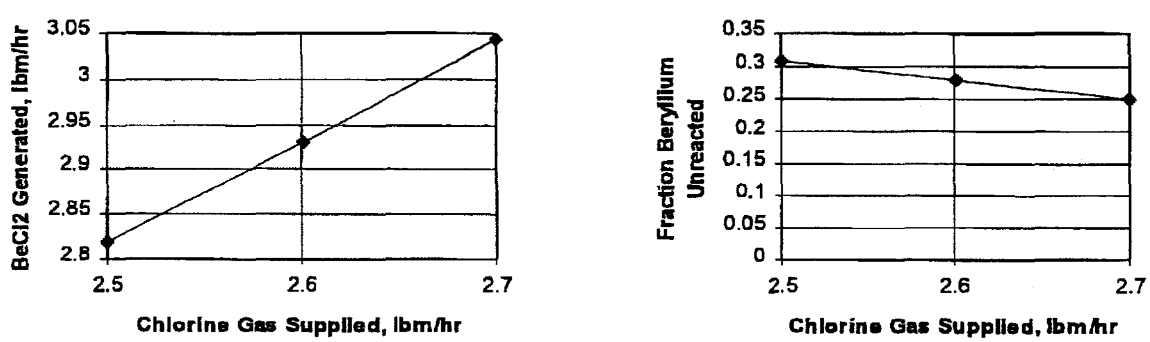

Figure 2. Beryllium Chloride Synthesis Simulation Results.

3. Beryllium Electrorefining

Electrorefining is a process that converts low purity feed into a high purity product. In the pilot process, a sacrificial anode was cast from low purity beryllium chips. This anode was placed in a conductive salt bath containing 10-weight percent $BeCl_2$ in a eutectic mixture of 50 weight percent potassium chloride (KCl) and 40-weight percent lithium chloride (LiCl). The KCl and LiCl concentrations in the eutectic are selected based on the eutectic melting point shown in Figure 3 [3]. The 355°C melting point corresponds to 58.5 mol % LiCl. An electrical current is applied across the bath, which causes the metals in the anode (beryllium and impurities) to ionize. The ions diffuse across the salt bath and are deposited as pure beryllium metal on a nickel cathode, which is also in the salt bath. The salt bath temperature was held at 500°C.

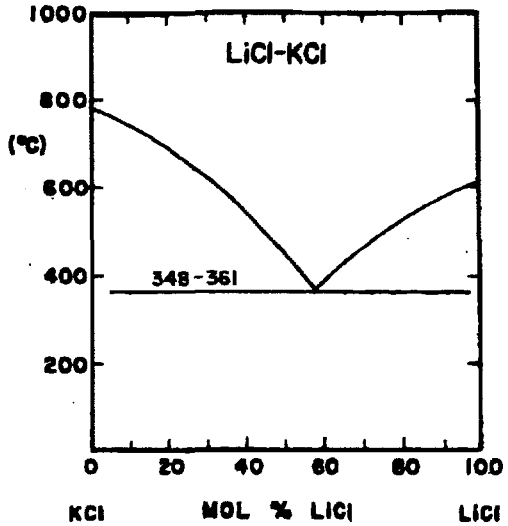

Figure 3. Potassium Chloride and Lithium Chloride Eutectic Phase Diagram

The simulation flow sheet for the electrorefining process is shown in Figure 4. Beryllium metal with aluminum, iron, magnesium, and silicone impurities (MET-IN) is contacted with the chlorine available (CL2-IN) in the salt bath using a Gibbs equilibrium reactor (RGIBBS) at a temperature of 500°C. The Gibbs free energy of the system is minimized establishing chemical equilibrium. From RGIBBS, in the diagram, vapors exit through the EXHAUST stream, solid metals and solid chlorides through the SOLIDS stream, and liquid chlorides and liquid metals through the TRANSFER stream to the stoichiometric reactor (RSTOIC) at 500°C. Complete dissociation of the chlorides in the TRANSFER stream occurs in RSTOIC. Therefore, the product stream, MET-OUT, will contain the purified solid metals and chlorine gas that result from the dissociation of the chlorides and liquid metal. The simulation shown in Figure 4 represents good approximation of a necessarily batch process by a steady-state simulator.

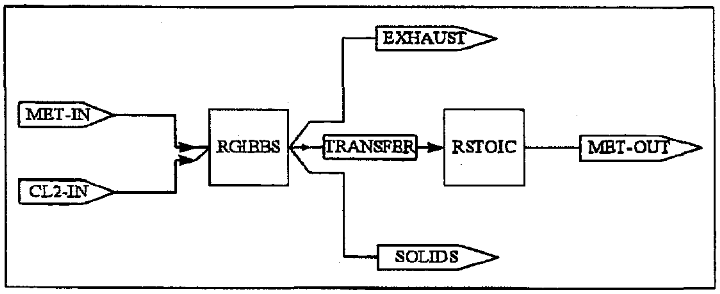

Figure 4. Beryllium Electrorefining Simulation Flow Sheet.

In these calculations, phase equilibrium had to be approximated for some compounds based on published freezing and boiling points because other thermodynamic data were not available. However, validity checks were made, and the simulator was able to calculate phase equilibrium for those materials, which clearly fell into the two-phase region. For example, beryllium chloride freezes at 405°C and boils at 520°C. The model was able to determine phase distributions for beryllium chloride.

The simulation results are close to the pilot plant data with aluminum impurities predicted to be 5 to 15 ppm, with only trace amounts of iron. Estimated recovery rates for beryllium, from the simulation, are shown in Figure 5. Several runs were made at temperatures ranging from 400 to 525°C. The data in Figure 5 predict more favorable recoveries at lower temperatures. One reason is that more beryllium chloride will enter the vapor phase as the temperature increases.

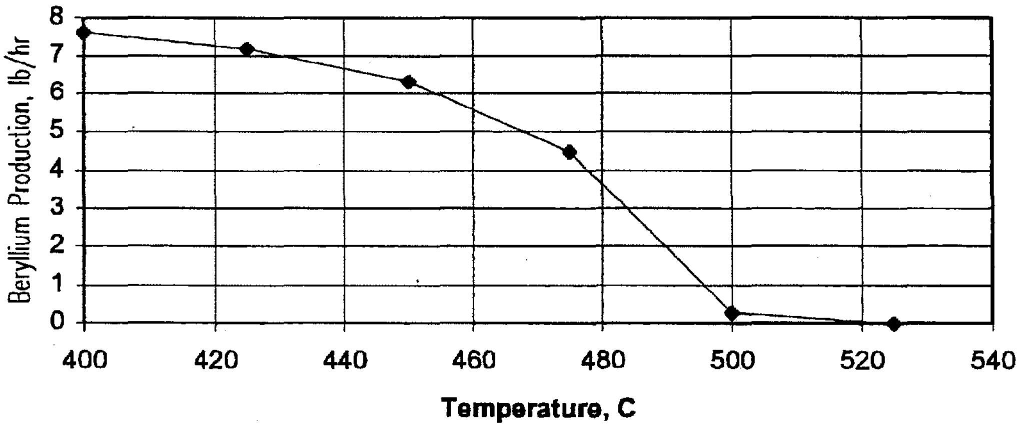

Figure 5. Beryllium Recovery Fraction (Based on Nine pounds/hr Feed Rate).

4. Conclusions

We have successfully modeled the semi-batch and batch processes necessary to electrorefine beryllium using a commercially available steady-state process simulator, AspenPlus. Results from simulating the first step, beryllium chloride synthesis, are in close agreement with the pilot plant operations. Results from simulating the second step, beryllium electrorefining, demonstrate better recovery efficiencies at lower temperatures. The thermodynamics of the problem depend upon both chemical and phase equilibrium, and we are continually trying to improve the model, even though it works quite well now. The major improvements will come through acquiring and implementing more and consistent fundamental physical and thermodynamic property data when they become available. A steady-state process would probably be a better choice for a production scale plant. We have created the tool necessary for that design.

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