POTENTIAL APPLICATION OF IONIC LIQUIDS IN ALUMINIUM PRODUCTION – ECONOMICAL AND ECOLOGICAL ASSESSMENT

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Aluminium is one of the most popular materials in the automotive, plane, ship, food and packaging industries mainly due to its light weight and corrosion resistance. The annual production of this metal is growing by 2% every year. The aluminium production technology applied in an industry is based on electrodeposition in cryolite in so called Hall–Héroult process. This process is considered very energy consuming and was proven to have considerably high negative environmental impact. However an alternative technology has been suggested in the literature since aluminium deposition has been successfully demonstrated with room temperature ionic liquids (RTILs) based on imidazolium, pyridinium and quaternary ammonium cations with AlCl₃ with an efficiency reaching almost 100%.

The aim of this paper is to perform a comparison of conventional Hall–Héroult process with new ionic liquid technology taking into account mainly the environmental and economical impact. As the result of our studies we came to the conclusion that ionic liquid’s application in aluminium production presents a very interesting alternative for technologies applied so far in the industry. However care must be taken when introducing ionic liquids to wide-scale use as their environmental impact is not fully acknowledged. In the process of industrial utilization of chemical substances a risk of unintentional release is always present and should be taken into account. Therefore, prior to the implementation of this new technology a full risk assessment, including potential adverse effects determination and estimation of mobility in all possible environmental compartments, is required.

key words: ionic liquids, aluminium production, global warming potential
INTRODUCTION

The natural resource for primary aluminium production is bauxite ore. Production involves two main stages: refining of alumina (aluminium oxide) form the ore in the Bayer’s process and then reduction of the oxide to metallic aluminium in the Hall-Héroult process. Due to its light weight and corrosion resistance, aluminium is one of the most popular materials in the automotive, plane, ship, food and packaging industries. Worldwide production has been growing continuously by 2% annually for the last 25 years to reach 28.9 kt in 2005 (Gielen 1998; Norgate, Jahanshahi and Rankin 2007). Generally, in the Hall-Héroult process alumina is dissolved in a molten cryolite ($\text{Na}_3\text{AlF}_6$) bath at 1000°C from which it is deposited by applying low voltage high electric current across carbon electrodes. In crude aluminium production energy costs is the key factor, as the Hall-Héroult process is known to be highly energy consuming (Gielen 1998). Moreover there are additional costs connected with aluminium production coming from a necessity to comply with environment protection regulations. They can be separated into two streams: first is a gaseous hydrofluoric acid (HF) and volatilized fluorides emission due to a hydrolysis reaction during the electrodeposition process. This can be almost completely prevented by either exchanging moisture bearing oxides for anhydrous ones or removing fluoride containing solvents. Otherwise it can also be decreased by constructing more efficient gas trapping devices. Another environmental issue is the emission of carbon dioxide during the production process. It has been calculated that more CO$_2$ than aluminium is produced from a mass unit of ore (Welch 1999). Due to these facts, extensive research for a better electrolyte which will allow for aluminium deposition at ambient temperatures and without formation of harmful substances is being conducted by a number of research groups (Yuguang and VanderNoot 1997; Jiang, Brym, Dubé, Lasia and Brisard 2006; Jiang, Brym, Dubé, Lasia and Brisard 2006). Electrodeposition from aqueous solutions is known to be inapplicable due to the aluminium reduction potential and hydrogen formation during the process (Abbott, Eardley, Farley, Griffith and Pratt 2001; Jiang, Brym, Dubé, Lasia and Brisard 2006). Organic solvents such as aromatic hydrocarbons or ethers were introduced as replacements of cryolite but were not considered superior due to their low conductivity, relatively narrow electrochemical window and the risk of self-combustion and potential explosion. Furthermore there are environmental issues connected with volatile organic compounds (VOC’s) application in industry as it is estimated that 20 billion kg of VOC’s are released to the atmosphere every year (Jiang, et al., 2006; Liu, Abedin and Endres 2006; Beaulieu, Tank and Kopacz 2008). In the 1980s, the application of a new type of solvents – ionic liquids (ILs) in aluminium production industry has been suggested and is continuously investigated up to date (Liu, Abedin and Endres 2006).
IONIC LIQUID’S POTENTIAL APPLICATION IN ALUMINIUM ELECTRODEPOSITION

Ionic liquids have melting points usually below 100°C due to large non-symmetrical organic cations. If they are substituted in place of cryolite, they have a significant potential to reduce the energy consumption of the aluminium production process. Additionally, ILs have a remarkably wide electrochemical potential window, often up to 5V. This property makes them particularly suitable for electrodeposition of metals and semiconductors as they do not undergo oxidation or reduction within the respective potential range (Baker, Baker, Pandey and Bright 2005; Frank and El 2006). Other advantages of IL application in aluminium production include: good solvent properties that allow for high concentrations of metals in the electrolyte, low vapour pressure limiting losses and air contamination, and good thermal and chemical stability (Moustafa, Abedin, Shkurankov, Zschippang, Saad, Bund and Endres 2007).

First aluminium electrodeposition from ILs to be reported in literature was the utilization of so-called first generation ILs which are a combination of AlCl$_3$ and organic chlorides (e.g. substituted pyridinium and imidazolium chlorides). The major drawback of those solvents was their hygroscopic nature due to which the whole process had to be conducted under an inert gas atmosphere. Additionally, the pyridinium cation is susceptible to reduction, and thereby it is narrowing electrochemical window of pyridinium based ILs (Jiang, Brym, Dubé, Lasia and Brisard 2006). Research groups attempted to change the anion to a more stable one such as: tetrafluoroborate (BF$_4^-$) or hexafluorophosphate (PF$_6^-$). Unfortunately these were proven to release HF after being exposed to the moisture. Third generation ILs – containing more hydrophobic anions, for example: trifluoromethanesulfonate (CF$_3$SO$_3^-$), bis(trifluoromethylsulfonyl)amide [(CF$_3$SO$_2$)$_2$N$^-$], or tris(trifluoromethanesulfonyl) methide [(CF$_3$SO$_2$)$_3$C$^-$], yield good quality aluminium deposits with no simultaneous solvent decomposition or toxic/dangerous side products evolving during the reaction (Abedin, Moustafa, Hempelmann, Natter and Endres 2005). In addition, the conductivity of ILs that can be applied in the Al industry is an order of magnitude lower than that of cryolite, but still higher than that of tetrahydrofuran or toluene (Liu, Yang and Zhang 2004). Albeit the low conductivity the temperature of the process would be two orders of magnitude lower that with cryolite. The electrodeposition of Al from AlCl$_3$ has a cell voltage of 3–3.4V (distance between plates of 10mm). The AlCl$_3$ required for this process is obtained from the chlorination of bauxite in the presence of carbon. The chlorine gas can be recycled from the electrolysis reaction of AlCl$_3$ to metallic Al and Cl$_2$ (Wu, Reddy and Rogers 2008).

It is commonly believed that ILs, mostly imidazolium and pyridinium based, are promising solvents for aluminium and other metals production on a wide scale. Nevertheless, there are still a few problems that need to be solved before their implementation in the industry. Those challenges are mainly: high cost of ILs
tation in the industry. Those challenges are mainly: high cost of ILs production, lower conductivity in comparison to cryolite (Edwards, Taylor, Russell and Maranville 1952) as well as lack of information about their environmental impact and chemical fate (Abbott, Eardley, Farley, Griffith and Pratt 2001; Abedin, Moustafa, Hempelmann, Natter and Endres 2005; Jiang, Brym, Dubé, Lasia and Brisard 2006). A broad range of international programs already exist which aim to protect humans health and the surrounding environment by introducing regulations concerning safe usage and management of chemical substances. The European Commission REACH system (Registration, Evaluation and Authorisation of Chemicals system) and United Nations Agenda 21, are two of the more significant ones, that attempt to gather information about the environmental impact and mobility, toxicity and contamination potential of chemicals used in industrial processes prior to their implementation. This knowledge is needed to provide defined set of information of the properties of chemical substances used and potential risk management strategies (United Nations Department of Economic and Social Affairs 2004; REACH 2007).

ENVIRONMENTAL IMPACT OF CONVENTIONAL ALUMINIUM PRODUCTION

The most significant disadvantage of the conventional Hall-Héroult process is its high energy demand. The theoretical minimum amount of energy required for the reduction of alumina to aluminium based on reaction enthalpy is 29.9 GJ/Mg of Al. However in real industrial aluminium refining processes, depending on the technology applied, 46 – 60 GJ/Mg is required. The high temperatures necessary to keep the cryolite molten is responsible for this large electricity demand. Although since the introduction of the process in 1886 significant improvements in energy efficiency have been made, the continually increasing prices of electricity have not allowed for major cost reductions of the production process (Gielen 1998).

The other important concern is environment pollution. Main air contaminants from aluminium production that might enter the atmosphere are: fluorides, perfluorocarbons (PFC), tars, polycyclic aromatic hydrocarbons, sulphur dioxide and other sulphur containing compounds, dust, metal containing compounds, nitrous oxides, and carbon mono- and dioxide. To decrease the melting temperature of a bath the fluoride compound, most often AlF$_3$, is added in a stoichiometric excess. The higher is the excess of AlF$_3$ the higher is the emission of fluoride to the atmosphere. Total fluoride formation from electrodeposition processes range from 20 kg to 40 kg of F/Mg of Al, after purification of effluent gases this values decreases to 0.4 kg – 1.0 kg of F/Mg of Al. Another dangerous substances evolved during electrodeposition process are perfluorocarbons, mainly tertafluoromethane and hexafluoroethane produced in a 10:1 ratio. Once produced, they cannot be removed from the gas stream by available tech-
nologies and their estimated atmospheric lifetime is approximately 50000 and 10000 years respectively. The so called “anodic phenomena”, responsible for their formation, are caused by a decrease of the amount of alumina in the bath below 1–2%. As the result voltage rises to reach the value that is high enough to cause the oxidation of fluoride components present in the bath on the anode and form PFC. The ILs that are suitable for aluminium production, based on the literature, are those containing halide alkylimidazolium and chloroaluminate mixture. During the electrodeposition of aluminium in these ILs the occurrence of PFC by anodic phenomena is not expected at all since there are no fluoride bearing compounds to be oxidised (Marks, Tabeereaux, Pape, Bakshi and Dolin 2001), however chlorine is still be produced. Due to the low temperatures the aluminium is electrodeposited on the cathode.

Technologically advanced production lines use semi-continuous automatic alumina feeding the bath which can significantly reduce PFC emissions to 0.02–0.1 kg PFC/Mg of Al (EU 2001). Technological modification of the arrangement of an electrodeposition cell for example by applying a Vertical Electrode Cell has the potential of cutting down energy demand by 15% and global warming potential by 35%, however other far more beneficial possibilities exist (Norgate, Jahanshahi and Rankin 2007).

In addition, the solid wastes generated during aluminium production in Hall-Héroult process present an environmental threat. Spent Pot Lining (SPL) is produced when the carbon refractory lining of an aluminium smelting pot reaches the end of its serviceable life. During its lifetime the cathode will crack and adsorb a high level of fluorides and cyanides. The contaminated pot lining has been classified as a hazardous waste material. Throughout decades, the amount of fluoride bearing waste generated is significant, considering that an average aluminium plant may have an annual production of 670 000 tons of aluminium (201 tons/year of fluoride bearing waste). Worldwide, quantities exceeding 500 000 tonnes a year of SPL are produced. A large majority of SPL is unprocessed, stockpiled or buried using licensed landfill sites. This type of disposal can have the potential of impacting on the environment. The leachate of such waste stockpiles can enter the ground and aquifers.

A variety of technologies exist which allow for safer disposal of SPL waste after aluminium production. These include utilising ion exchange to remove fluoride from the leachate (Singh, Kumar, Sen and Majumdar 1999), by integration into cement (Silveira, Dantas, Blasques and Santos 2002), or by oxidation of the graphite (Mazumder 2003). The inclusion of IL into the electrolytic mixture might influence the effectiveness of any or all of these waste disposal methods for the SPL waste. However a number of these methods, for example, the immobilisation by cementing, have been shown to be effective also with some organic compounds. It is therefore not unfeasible that IL can be included in the electrolytic mixture, and the resultant SPL waste, containing IL, may still be disposed of safely.
ENVIRONMENTAL IMPACT OF IONIC LIQUIDS

ILs are known to be non-volatile and thus to have low potential for atmospheric contamination or intoxication of humans by inhalation. However ILs posses the potential of soil and water contamination as they might be water soluble and can be sorbed onto solids. Their unintentional release to the environment can create a threat to human and animal life or health and as such should be by all possible means prevented. Limited research has been done in the field of ILs environmental fate assessment and more knowledge is urgently required (Jastorff et al., 2003). One of the most crucial issues in ecological risk assessment of ILs is the determination of their bioavailability and mobility in aquatic and terrestrial ecosystems. Due to the hydrophobicity of alkyl substituents and the positive charge (e.g. as a delocalised charge on the imidazole ring), ILs can be sorbed to organic matter and minerals by van der Waals forces and electrostatic interaction respectively; moreover there is the possibility of hydrogen bond formation between hydrogen atoms of ILs and polar moieties of soil organic matter. Finally the given three mechanisms combine together resulting in higher net sorption (Beaulieu, Tank and Kopacz 2008). The strength of sorption will determine the potential of soil and water contamination. Strong bonding to soil particles or organic matter can prevent leaching to groundwater which can further cause drinking water contamination. It can also decrease toxicity for flora and fauna since bound chemicals are not available for uptake. Similarly partitioning between sediments and water bodies will decrease toxicity towards aquatic organisms (Matzke, Stolte, Arning, Uebersa and Filser 2008).

Several research groups investigated the phenomenon of sorption of ILs onto soils and minerals. The overall conclusion was that dialkylimidazolium ILs are unlikely to be retarded in most geological systems to a large extent, taking into account also bacterial community, unless significant amount of clay or organic matter is present. Consequently they possess a potential to enter ground water systems and to act as contaminants. It was also confirmed that sorption can be altered by pH of soil since the more acidic the soil solution the less negatively charged active sites are available, and the lower is the cation exchange capacity (CEC). Thus decreasing the pH of soil/solution can cause desorption of ILs already immobilized by soil and their leaching. Furthermore ionic strength of solution was proven to influence sorption due to the competition of ILs cations and salt cations for negatively charged active sites of solids (Stepnowski, Mrozik and Nichthauser 2007). Data obtained independently by Stepnowski and Matzke stated that more hydrophilic ILs (with shorter alkyl side chain) would be more mobile in the environment than hydrophobic ones due to a reduced amount of possible interactions with soil/organic matter system since organic substances present in soil were proven to be responsible for ILs retention, however interaction by ion exchange is also playing a role in the sorption process (Stepnowski 2005; Matzke, Stolte, Arning, Uebersa and Filser 2008). Exact sorption
mechanisms have not been described yet since there are discrepancies in the result of sorption experiments by a number of researchers (Markiewicz, Biedrzycka and Bielecka 2006). It is also not possible to unequivocally state what parameter of the system are influencing sorption of ILs in the environment (Gorman-Lewis and Fein 2004; Stepnowski 2005; Stepnowski, Mrozik and Nichthauser 2007; Beaulieu, Tank and Kopacz 2008)

FROM AN ECONOMICAL POINT OF VIEW

Total energy demand for primary aluminium production is approximately 170 GJ/Mg, 16–20% of this energy is required for Bayer’s bauxite ore refining whereas as much as 65% is needed for aluminium electrodeposition in Hall–Héroult process (Gagnea and Nappi 2000). About 60% of electricity used in aluminium production comes from hydroelectric power (Moors, Mulder and Vergragt 2005). The source of energy powering the electrolytic bath is an important factor from an environmental point of view since the carbon dioxide emission can vary by a factor of five depending on whether coal or hydroelectricity was used. Substitution of cryolite with ionic liquids not only has a potential of decreasing energy demand but could also prevent the emission of greenhouse gases to the atmosphere. Common enterprise of industry and academia in Australia, which is one of the biggest aluminium producers, revealed that application of ionic liquids might cut down the electricity cost of Hall–Héroult process by 30% as well as reduce atmospheric emission (Nogrady 2006)

The substitution of cryolite with ILs is beneficial from the economical and environmental point of view. To obtain a clear comparison of environmental and economical parameters of aluminium production in standard Hall–Héroult and ionic liquids utilizing processes we prepared Figure 1.

Significant energy demand reduction is possible due to lower temperature required during electrolysis in IL. Since electricity costs are a key factor for aluminium production, energy input reduction can provide significant savings. Energy demand is also influencing global warming potential (GWP) of the process since energy needed for heating the electrolytic bath can also result in CO₂ production. Taking into account that almost 40% of energy for smelting comes from coal burning power plants the possibility of IL’s application in aluminium industry offers a GWP as well as costs reduction potential (Moors, Mulder and Vergragt 2005). Additionally a considerable decrease in harmful gas emission might be achieved when fluoride bearing electrolyte is excluded from the process. As shown on Figure 1, their evolution to the atmosphere can be avoided by performing electrolysis in a non-fluoride IL. The influence of aluminium production technology on global warming potential was divided into two parameters: GWP of smelting process and total GWP. The first one is describing reduction of possible adverse effects due to mainly PFCs emission elimination. Knowing that greenhouse impact of those pollutants is exceeding CO₂ global
warming potential by a factor of 6500 and 9200 respectively and mass released per kg of Al we calculated the GWP due to PFCs formation as \( \text{CO}_2 \) mass equivalents. The greenhouse impact of other gases is negligible in comparison to PFCs thus taking only those entities into account provides a good estimation of GWP (EU 2001). The total GWP includes emission of greenhouse gases during aluminium production, starting from extraction of alumina from bauxite ore to electrolytic separation of aluminium (Norgate, Jahanshahi and Rankin 2007). Air emission presented on the graph is taking into account amount of PFCs released in a form of \( \text{CF}_4 \) and \( \text{C}_2\text{F}_6 \). IL’s toxicity measured as a \( \text{LD}_{50} \) value in acute toxicity test of \textit{Daphnia sp.} is lower than cryolite’s which allows for safer handling.

Fig. 1. Comparison of economical and environmental factors in aluminium production by Hall-Herault process (---), and ILs utilizing process (-----)
CONCLUSIONS

Electrodeposition of aluminium from ionic liquids was proven, presenting a promising alternative to the high cost and high environmental impact production by standard Hall-Héroult process. From present analysis it can be seen that introduction of ionic liquids to aluminium smelting can be beneficial for environmental and economical point of view.

Current research conducted into the phenomenon of ILs sorption to soils gives different, sometimes contradictory results. Even in simplified, artificial systems like one applied by Gorman – Lewis and Fein no clear answer for the question: “What is the mechanism of ILs sorption?” could been obtained. Together with complicating the matrix, in order to simulate environmental conditions, more sorption mechanisms have to be taken into account and results become even more ambiguous.

Regardless of the level of uncertainty considering sorption strength one have to bear in mind that all the benefits connected with its application joined with the proper handling and usage management can introduce a significant improvement in economy and ecology of aluminium production. Additionally, according to predictions available up to date, ILs are not much more dangerous that cryolite although they are definitely less recognised.

REFERENCES


Ze względu na swój niewielki ciężar właściwy oraz odporność na korozję aluminium jest jednym z najczęściej wkorzystywanych materiałów w przemyśle samochodowym, lotniczym, stoczniowym, spożywczym i w produkcji opakowań. Produkcja tego metalu rośnie o 2% w skali roku. Technologia wytwarzania aluminium stosowana na skalę przemysłową oparta jest na elektrodepozycji w ciekłym kriolicie i nosi nazwę procesu Hall-Heroult’a. Technologia ta wymaga wysokich nakładów energii elektrycznej, charakteryzuje się ponadto, szeroko udokumentowanym, negatywnym wpływem na środowisko naturalne. Produkcja aluminium możliwa jest również z wykorzystaniem innych technologii, jako że istnieją doniesienia literaturowe na temat elektrodepozycji aluminium z mieszaniny cieczy jonowych zawierających w rdzeniu imidazol, pirymidynę lub czwartorzędową sól amoniową oraz AlCl₃, w temperaturze zbliżonej do pokojowej z efektywnością sięgającą niemal 100%. Celem niniejszej publikacji jest dokonanie porównania obu wspomnianych technologii pod względem wpływu na środowisko oraz ekonomii produkcji.

W wyniku przeprowadzonych studiów doszliśmy do wniosku, iż zastosowanie cieczy jonowych w produkcji aluminium stanowi interesującą alternatywę dla dotychczas stosowanego procesu Hall-Heroult’a. Niemniej jednak wprowadzenie tych nowych mediów do produkcji na szeroką skalę towarzyszy powinna nadzwyczajna ostróżność jako że wpływ tycząc związków na środowisko nie został w pełni poznany. W procesie przemysłowego użytkowania związków chemicznych ryzyko ich niezamierzonego uwolnienia musi być brane pod uwagę. Z tego względu przed wprowadzeniem tej technologii produkcji aluminium należy dokonać pełnej analizy ryzyka, uwzględniając ewentualny negatywny wpływ na środowisko jak również oraz zidentyfikować potencjalne rozmieszczenie w różnych elementach ekosystemów.

słowka kluczowe: cieczy jonowe, produkcja aluminium, potencjał tworzenia efektu cieplarnianego