Proceedings of the International Conference on Mining, Material and Metallurgical Engineering
Prague, Czech Republic, August 11-12, 2014
Paper No. 60

Preliminary Investigation of Ionic Liquids Utilization in Primary Aluminum Production

N. Poulimenou, I. Giannopoulou, D. Panias
National Technical University of Athens, School of Mining and Metallurgical Engineering,
9 Iroon Polytechniou Str., 15780 Zografou Campus, Greece
nickyliana@hotmail.com

Abstract - Today, the primary production of aluminium is based on two processes: (a) the Bayer Process and (b) the Hall-Heroult Process. Both methods deal with some economic and environmental drawbacks. The aluminium production is an energy intensive process consuming 53-61 GJ/ t of aluminium while huge amount of red mud and gaseous emissions are inevitably produced through the whole process.The utilization of a new family of solvents called Ionic Liquids (IL) in the primary aluminum production is the subject of this paper which examines the possibility of directly dissolving metallurgical alumina, trihydrated alumina and bauxite in 1-Ethyl-3-methyl-imidazolium hydrogen sulphate ([Emim]HSO_4). The results show that alumina can be dissolved relatively easily in this ionic liquid at 210^{o}C forming a melt that contain 9% w/w alumina which is higher than the alumina content in Hall-Heroult melts. Bauxites can also be directly dissolved in this ionic liquid with iron exhibiting higher dissolution than aluminium while silicon dissolution is negligible.

***Keywords*:** Ionic liquids, ([Emim]HSO_4), Alumina, Trihydrated alumina, Bauxite.

1. Introduction

Over the last century, the production of aluminum is based on two metallurgical processes, the Bayer Process and the Hall-Heroult Process. The Bayer process (Web-1) consists of four basic steps using bauxite as raw material. The aluminum is selectively extracted from its ore by a moderately concentrated sodium hydroxide solution (digestion step) for the production of hydrated alumina ($Al(OH)_3$), which is the intermediate product (precipitation step). The final product aluminium oxide (Al_2O_3) is produced by the decomposition of hydrated alumina in high temperatures (calcination step). Bayer process provides alumina as raw material for the electrolysis of aluminum by the Hall–Héroult process.

Both methods deal with some economic and environmental issues. Specifically, the production of one tonne of aluminium requires the consumption of energy ranging between 53 and 61 GJ, according to the electrolysis cell, same energy as a small town needs (Bref document, 2001). As far as the environmental impact is concerned, the Bayer process and the Hall-Heroult process burden the environment by depositing huge amount of red mud and by producing gaseous & solid wastes, respectively.

The possibility of applying these salts, called ionic liquids (ILs) has been studied only in experimental way in the metallurgy of non-ferrous metals. Ionic liquids are considered to be the most promising possible extracting agents studied over the last years, due to their low toxicity and the imperceptible environmental impact they cause. The application of ionic liquids as solvents in extractive metallurgy may offer potential environmentally sensitive procedures and alternatives to hydrometallurgical processes.

Ionic liquids are organic salts, with a melting point that lies below 100 ^{o}C. The low melting point in ionic liquids is attributed to reduced symmetry causing frustration of crystallinity (Kirk-Othmer Encyclopedia). Ionic liquids consist of a bulky organic cation and a smallest organic or inorganic anion (Ullmann’s Encyclopedia). The variability, the combination, the position and the size of the anions and the cations adjust the remarkable properties, that ionic liquids have (Ullmann’s Encyclopedia), such as a low vapour pressure, a high thermal and chemical stability, a wide range for the liquid phase, an ability to dissolve of a wide range of inorganic and organic compounds, high electrical conductivity and a broad electrochemical window (Abbott et al., 2011).

The basic idea behind this research was to find a method that will allow the recovery of reactive metals such as aluminum from a non-aqueous solution at low temperatures and ambient conditions. For this reason the current study examines the possibility of directly dissolving metallurgical alumina, trihydrated alumina and bauxite in an ionic liquid of the imidazolium family namely 1-Ethyl-3-methyl-imidazolium hydrogen sulphate [Emim]HSO_4.

2. Experimental

2.1. Materials

All the chemicals used in this study were of analytical grade. Alumina, hydrated alumina (powder) and bauxites samples (one gibbsitic and one diasporic) were provided by the Greek Industry "Aluminium S.A.". The samples characterization was realized through chemical analysis (XRF and fusion/dissolution), mineralogical analysis (XRD), particle size analysis, density measurements and specific surface area measurements.

All samples were dried in an oven at 105 °C to remove the moisture content. The wet chemical analytical technique used in this study, combines fusion (1000 ^oC) of the solid samples with a mixture of $LiBO_4/KNO_3$, followed by nitric acid dissolution. The metal content in the produced solution was determined by Atomic Absorption Spectroscopy (AAS). The results of both analytical techniques, for the four solids, are shown in Table 1. According to Table 1, both alumina and hydrated alumina are principally composed of Al_2O_3. As far as concerned bauxites, they are principally composed of Al_2O_3 and Fe_2O_3, while the most important occurring impurities are SiO_2 and TiO_2. Table 1 also shows the loss on ignition (LOI) for the four solids.

Table 1. Chemical analysis of alumina, hydrated alumina, gibbsitic and diasporic bauxite.

	Al_2O_3	Na_2O	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	LOI
Alumina(1)	99.6	<0.4	-	-	-	-	-	-
Hydrated Alumina(1)	68.23	0.4	-	-	-	-	-	31.37
Gibbsitic bauxite(2)	47.40	-	1.87	26.99	2.29	0.24	0.06	21.12
Diasporic Bauxite(2)	51.48	-	2.57	31.75	3.43	0.86	-	9.90

The mineralogical analysis of the four solid samples was performed according to the X-Ray Diffraction method. Hydrated alumina is consisted of gibbsite ($Al(OH)_3$), whereas alumina is consisted of corundum-alpha (Al_2O_3) and aluminium oxide-gamma (γ-Al_2O_3). As far as concerned bauxites, the main phase of gibbsitic bauxite is gibbsite ($Al(OH)_3$), while the secondary phases are hematite (Fe_2O_3) and boehmite (γ-AlO(OH)). In diasporic bauxite, the mineralogical phases of diaspore (α-AlO(OH)) and boehmite (γ-AlO(OH)) predominate; furthermore, some secondary mineralogical phases are detected, such as hematite (Fe_2O_3) and anatase (TiO_2). The results of the mean particle size, specific surface area and density measurements are shown in Table 2.

Table 2. Physical properties of alumina, hydrated alumina and bauxites.

	Particle Size d_{50} (μm)	Specific Surface Area (m^2/g)	Density (kg/m^3)
Alumina	88.19	82.52	4039
Hydrated Alumina	96.93	49.17	2504
Gibbsitic bauxite	62.50	10.46	2680
Diasporic bauxite	72.31	11.53	3490

The ionic liquid [Emim]HSO_4 was used without any further purification. The characterization of ionic liquid includes density measurements, viscosity measurements and thermogravimetric analysis. The density and viscosity measurements of the ionic liquid at various temperatures are shown in Table 3.

---

(1) Wet -chemical analysis
(2) XRF-analysis

Table 3. Density and viscosity measurements of [Emim]HSO_4.

Temperature (^oC)	Density (kg/m^3)	Viscosity (mPa s)
25	1367	-
30	1342	1150
60	1330	225
90	1318	105

The results of the thermogravimetric analysis shown that the thermal decomposition of [Emim]HSO_4 starts after the temperature of 300 ^oC.

2.2. Experimental Methods

The first group of experiments investigated the extraction of aluminium from Al_2O_3, using the ionic liquid [Emim]HSO_4. In this group of experiments, the effect of temperature, retention time, and addition of water (direct and indirect) on the dissolution of Al_2O_3 in [Emim]HSO_4 was studied. All experiments were conducted in a glass reactor that was placed on a heated plate, thermostatically controlled by a thermocouple; the *Al_2O_3 / [Emim]HSO_4* system formed in the reactor was agitated through a magnetic stirrer over the range of 800 - 850 rpm. Reactor was operated under atmospheric pressure (open reactor) due to the negligible vapour pressure of [Emim]HSO_4. In each experiment, 1 g of Al_2O_3 and 20 ml of [Emim]HSO_4 were used.

As far as concerned the effect of temperature, seven experiments were conducted at the temperatures of 70, 90, 120, 150, 180, 210 and 240 ^oC; the duration of each experiment was 24 hours. The effect of time on the dissolution of Al_2O_3 in [Emim]HSO_4 was tested in two different temperatures. Specifically, three experiments were conducted at the temperature of 210 °C for 24, 48 and 96 hours and two more experiments at the temperature of 240 °C, for 24 and 48 hours. The first group of experiments comes to an end by studying the effect of adding water in the system of *Al_2O_3 / [Emim]HSO_4*, directly and indirectly. Directly, by adding D.I. water in [Emim]HSO_4, so as the content of the ionic liquid in the resulted aqueous solutions to be 75% or 50% (v/v). Indirectly, through the use of hydrated alumina instead of alumina.

The second group of experiments investigated the extraction of aluminium from bauxite ores. In each experiment of this group, a volume of 20 ml of [Emim]HSO_4 was used, in which 1.66 g of diasporic bauxite or 1.87 g of gibbsitic bauxite were added; the quantities of both solids are equivalent to 1 g Al_2O_3, according to the chemical analysis given in Table 1. Two different temperatures were tested per bauxite, 150 and 210 ^oC; the duration of each test was 24 hours.

3. Results and Discussion

3.1. The Dissolution of Aluminium from Al_2O_3

The research on the dissolution of aluminium from Al_2O_3 in the ionic liquid [Emim]HSO_4 focused on the effect of the temperature, the time and the presence of water. The dissolved aluminium is expressed as mass (g) of Al_2O_3 per volume (L) of ionic liquid.

3.1.1. Effect of Temperature

The results of alumina leaching in [Emim]HSO_4 at seven different temperatures, varying from 70 to 250 ^oC, are given in Fig 1. As shown in Fig 1, the rate of alumina dissolution increased almost linearly with the temperature. This rate was low at temperatures lower that 150 ^oC and higher than 180 ^oC. In-between the temperatures of 150 and 180 ^oC, the rate of Al_2O_3 dissolution increased impressively, indicating the need of moderately high temperatures for the process. At temperatures lower than 150 ^oC, the alumina content in the ionic liquid (IL) (% w/w) was below 0.28%, which is substantially lower than the composition of molten cryolite (1 - 6%) in Hall-Heroult process. At temperatures higher than 180 ^oC, the alumina content in IL varied in-between 1.32 - 1.7%, which lies above but close to the lowest composition of molten cryolite in the current industrial practice.

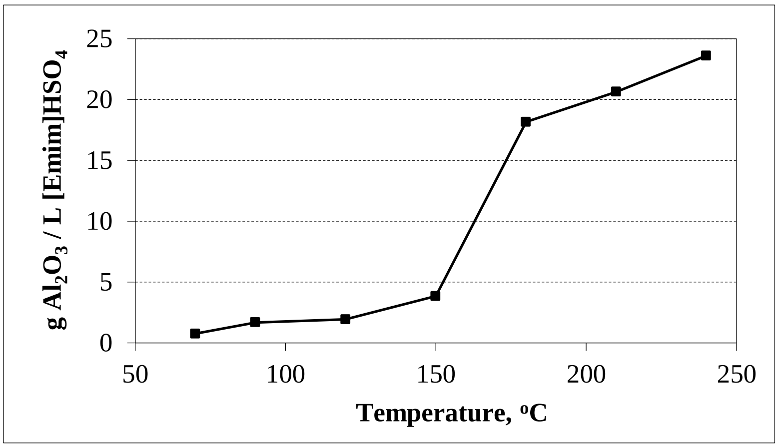

Fig. 1. Dissolution of Al_2O_3 in the ionic liquid [Emim]HSO_4 (w/v) versus temperature (retention time = 24 h).

The evident increase of the Al_2O_3 dissolution in the ionic liquid with the temperature increase from 150 °C to 180 °C, from 3.84 g/L to 18.17 g/L, respectively, may be ascribed to the important increase of the [Emim]HSO_4 viscosity, at temperatures higher than 150 °C.

The temperature-dependence of the viscosity of [Emim]HSO_4 could be mathematically studied by the Arrhenius equation, $n = n_o \cdot e^{E_n/(RT)}$, where n_o is the pre-exponential factor, E_n is the activation energy, R is the universal gas constant and T is the temperature. Taking the natural logarithm of Arrhenius' equation yields Eq. (1) that permits the determination of the equations' parameters by means of linear regression, through experimental measurements of viscosity versus temperature.

$$\ln(n) = \ln(n_o) + \frac{E_n}{RT} \qquad (1)$$

The linear fit of the experimental measurements shown in Table 3 is presented in Fig. 2. The linear regression resulted in the determination of the the parameters of the Arrhenius equation as follows: n_o = 4.39 x 10^{-4} mPa s and E_o = 34.40 kJ/mol.

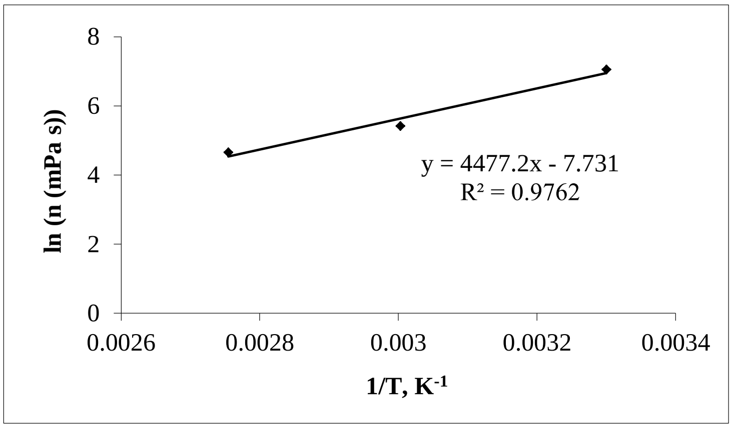

Fig. 2. Linear fit of the experimental measurements of viscosity, versus temperature.

The Arrhenius plot obtained, based on the above experimentally estimated parameters, is shown in Fig. 3. It could be seen in Fig. 3 that the viscosity is markedly affected by the temperature. As the temperature increases, the viscosity of [Emim]HSO_4 decreases from 189.5 mPa s at 70 °C to 16.5 mPa s at 150 °C, improving substantially the alumina dissolution in this temperature region (Fig.1). At 180 °C the viscosity is 8.3 mPa s, which is the half of the value it has at 150 °C, while at 240 °C, it is 2.6 mPa s, which is almost at the same order of magnitude with the viscosity of water at 20 °C (1 mPa s). Therefore, the increase of temperature at values higher than 180 °C decreases the viscosity of the ionic liquid at values closer to the water viscosity at ambient temperature, improving this way the solid particles wettability from the IL, decreasing the diffusion resistance and rendering the dissolution process faster, as is seen in Fig. 1.

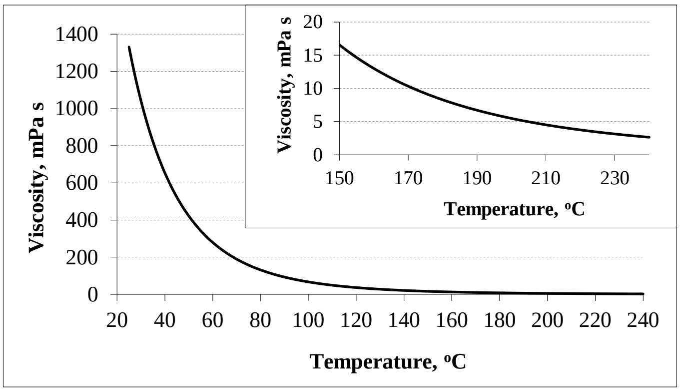

Fig. 3. Arrhenius plot of the viscosity of the ionic liquid [Emim]HSO_4, versus temperature.

3.1.2. Effect of Time

The kinetic behavior of alumina dissolution in [Emim]HSO_4, as is seen in Fig. 4, follows a typical pattern. The dissolution rate is high at the first stages and then decreases gradually, as the time is passing, approaching slowly an equilibrium stage, which is dependent on process temperature.

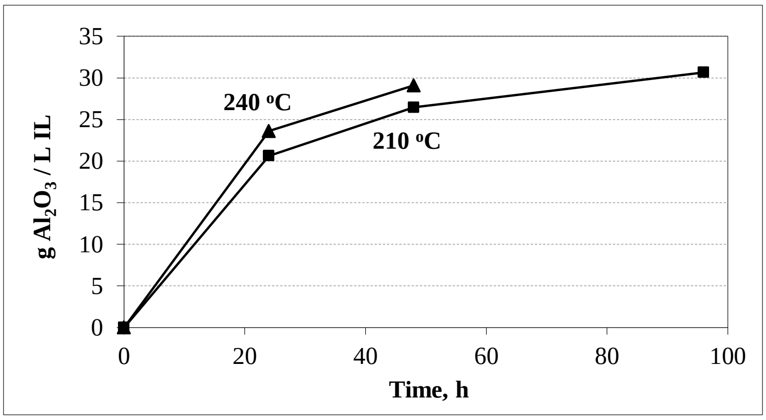

Fig. 4. The dissolution of Al_2O_3 in the ionic liquid [Emim]HSO_4 (w/v) versus time.

3.1.3. Effect of the Presence of Water

The effect of the water addition on the dissolution of Al_2O_3 in [Emim]HSO_4 was studied at 90 °C, in order to avoid the water evaporation phenomena in the open reactor used. The results of this study are shown in Fig. 5 and indicate a substantial increase of alumina dissolution with the water addition. Indeed, alumina dissolution has increased 7-folds as the water to IL volume ratio increases from 0 to 1.

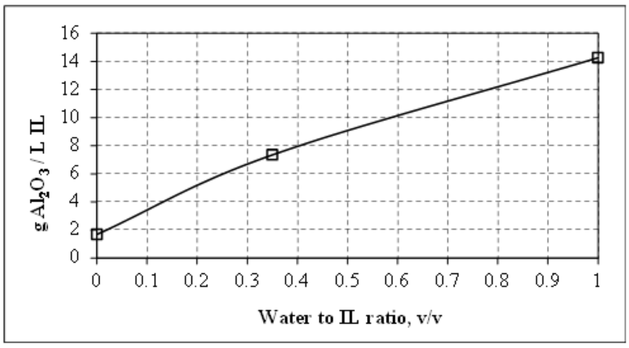

Fig. 5. Dissolution of Al_2O_3 in [Emim]HSO_4 versus water content (% v/v). Experimental conditions: 90 °C, 24 h

The addition of water in the *Al_2O_3 / [Emim]HSO_4* system acts as a catalyst in the reaction of dissolution of aluminium oxide in the ionic liquid [Emim]HSO_4. The addition of water (a) reduces the viscosity of the liquid phase, improving substantially the particles wetting by the solvent and the diffusion phenomena from and to the alumina particles, (b) hydroxylates the surface of alumina's grains, affecting positively its dissolution, (c) increases substantially the free protons concentration in the leaching agent through the dissociation of HSO_4^- and thus, activates the mechanism of proton assisted dissolution of oxides and finally (d) activates the ligand SO_4^{2-} promoting the dissolution mechanism of alumina, through the complexation of Al with SO_4^{2-}. All the above contribute to the dissolution mechanism, so that the dissolution of alumina to accelerate significantly and to reach high levels at very moderate experimental conditions.

Although the low boiling point of water limited the research at very low temperatures (<100 °C), where the leaching efficiency of IL is very low (Fig 1), an additional investigation took place at the temperature of 210 °C, studying the dissolution of hydrated alumina, with the form of gibbsite $Al(OH)_3$, in the pure IL. Following this experimental set up, water is added indirectly in the system through the already hydroxylated surface of gibbsite particles. At 210 °C and after 24 h, the hydrated alumina was significantly dissolved in the ionic liquid [Emim]HSO_4, since the amount of Al_2O_3 dissolved in the IL was 125.65 g/L, which is extremely high, in comparison to the non-hydrated alumina dissolved at the same experimental conditions Fig 6.

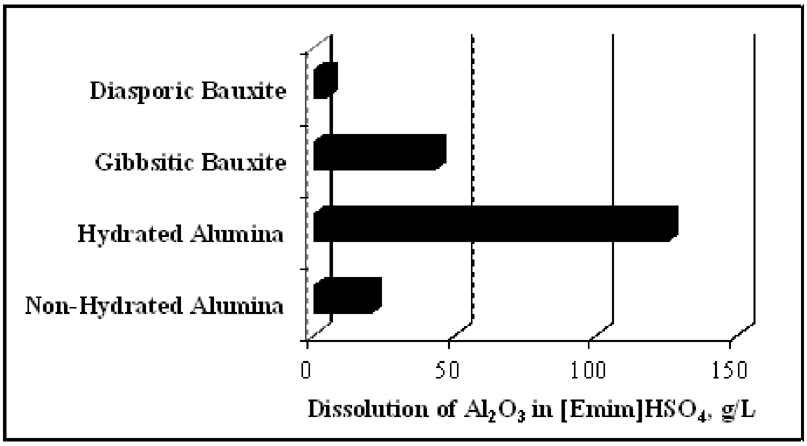

Fig. 6. Comparison of Al_2O_3 dissolution from several mineralogical phases in [Emim]HSO_4 at 210 °C and 24 h.

The hydroxylated surface of the particles of $Al(OH)_3$ improves substantially the dissolution of aluminium in the pure IL. Under those conditions, the Al_2O_3 content in the ionic liquid reached the value of 9.19% (w/w), which is about 1.5 times higher than the maximum content of Al_2O_3 in the molten cryolite of the currently used industrial Hall-Heroult process. This is a sound result because it opens a new route for the electrolytic production of aluminium from ionic liquids based on the hydrated alumina instead of the metallurgical alumina. Following this way, the Bayer process has to be modified by omitting the energy intensive calcination stage with profound effects on its energetic, economic and environmental performance.

3.2 Dissolution of Bauxites

Gibbsitic and diasporic bauxites were leached in the ionic liquid [Emim]HSO_4 at temperatures varying from 150 to 210 °C, under atmospheric conditions, for 24 hours. According to the experimental results shown in Fig. 7, the dissolution of the three basic components of bauxites, Al_2O_3, Fe_2O_3 and TiO_2, is affected by the temperature increase for both types of bauxites. The dissolution of Al_2O_3 is also affected by the type of bauxite; Al_2O_3 is dissolved substantially easier from the gibbsitic rather than the diasporic bauxite. At 210 °C, 87% of the alumina contained in the gibbsitic bauxite was dissolved in the ionic liquid, while from the diasporic bauxite, only 10% of the contained alumina was dissolved in the same IL. On the contrary, Fe_2O_3 dissolution was not affected by the type of bauxite. At 210 °C, 94% of Fe_2O_3 contained in the gibbsitic bauxite and 79% of that contained in the diasporic one was dissolved. Finally, TiO_2 is not easily dissolved in the [Emim]HSO_4 from both types of bauxites, reaching quite low dissolved quantities at 210°C around 10% of the bauxites' TiO_2

content. Under the studied experimental conditions, silica was not dissolved in the IL from both types of bauxite.

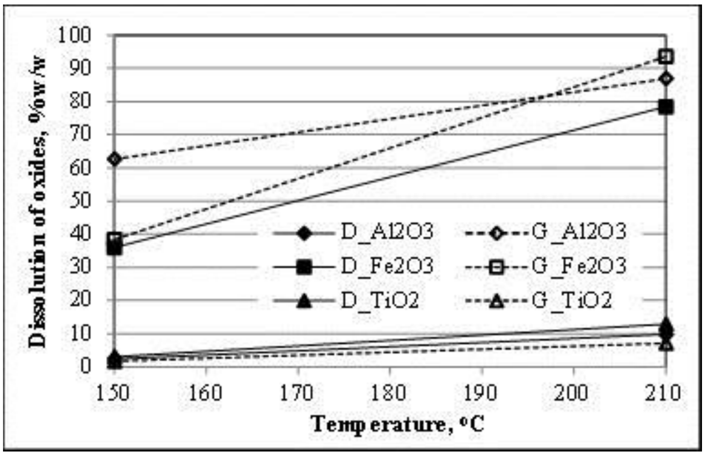

Fig.7. Dissolution of Al_2O_3, Fe_2O_3 and TiO_2 from both types of bauxite in [Emim]HSO_4, versus temperature (Retention time= 24 h, G= Gibbsitic Bauxite and D= Diasporic Bauxite).

The preliminary results from the dissolution of the oxides contained in gibbsitic bauxites show that it is feasible to leach the iron and aluminium with the [Emim]HSO_4, without appreciable co-dissolution of Ti and Si. According to the same results, the diasporic bauxite shows different behaviour, concerning the dissolution of alumina in the [Emim]$HSO_{4,}$ which was substantially lower, compared to that of the gibbsitic bauxite. Thus, further work is required to evaluate the dissolution mechanism of Al_2O_3 and Fe_2O_3 in the ionic liquid [Emim]HSO_4 in order to optimize the process of their extraction with such leaching agents. In such a case, a new process for the co-production of iron and aluminium from the bauxitic ores could be arisen, by replacing the Bayer process with that of using ionic liquids as leaching agents. Such a process has a tremendous interest for the primary alumina and aluminum industry with some profound advantages, the most important of which is the elimination of the red mud waste.

4. Conclusion

The main conclusion of the performed investigation is, that the [Emim]HSO_4 can be an alternative and effective solvent for the dissolution of aluminium from oxidic phases. The dissolution of metallurgical alumina reached 30.66 g per liter of IL at 210 ^oC and after 96 h. At the same temperature, hydrated alumina is dissolved substantially easier and reached after 24 h the very high concentration of 125.65 g of Al_2O_3 per liter of [Emim]HSO_4,.

Gibbsitic bauxites are in general, more effectively leached in [Emim]HSO_4, in relation to the diasporic ones. At 210 ^oC and after 24 hours, 87% of Al_2O_3 and 94% of Fe_2O_3 contained in the gibbsitic bauxite were leached. At the same conditions, the Al_2O_3 leached from the diasporic bauxite was only 10%, while the leached Fe_2O_3 reached 79%. Finally, the co-dissolution of Ti and Si from bauxites in [Emim]HSO_4 was very low; lower than 10 % in case of titanium and not appreciable, in case of Si.

References

A. P. Abbott, G. Frisch, J. Hartley & K. S. Ryder (2011). Processing of metals oxides using ionic liquids, Green Chemistry Vol. 13, pp 471-481.

EUROPEAN COMMISSION (2001). Integrated Pollution Prevention and Control (IPPC) reference document on best available techniques in the non ferrous metals industries, Chapter. 4, pp. 284.

Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons Ed., Vol. 26: Ionic Liquids, pp. 836.

Ullmann’s Encyclopedia of Industrial Chemistry, Willey-VCH Ed., Vol. 19: Ionic liquids, pp. 548.

Web sites:
Web-1: http://www.metal.ntua.gr/index.pl/notes7d2d23d9_gr consulted 11 June 2012.