Article

Efficiency of Sulfuric Acid on Selective Scandium Leachability from Bauxite Residue†

Maria Ochsenkuehn-Petropoulou*, Lamprini-Areti Tsakanika*, Theopisti Lymperopoulou, Klaus-Michael Ochsenkuehn, Konstantinos Hatzilyberis, Paraskevas Georgiou, Chrysanthos Stergiopoulos, Olga Serifi and Fotis Tsopelas

School of Chemical Engineering (Chem Eng.), National Technical University of Athens (NTUA), 9 Iroon Polytechniou St., 15780 Athens, Greece; oxenki@central.ntua.gr (M.O.-P.), btsakanika@gmail.com (L.-A.T.), veralyb@chemeng.ntua.gr (T.L.), klausochsenkuehn@yahoo.com (K.-M.O.), ksh@chemeng.ntua.gr (K.H.), pngche@gmail.com (P.G.), chrisxp3@hotmail.com (C.S.), olga.serifi@gmail.com (O.S.), ftsop@central.ntua.gr (F.T.)

* Correspondence: oxenki@central.ntua.gr (M.O.-P.) Tel.: +30-210-7723094, +30-6972035984 and btsakanika@gmail.com (L.-A.T.) Tel.:+30-210-7724022, +30-6955239222

† This paper is part of the oral presentation entitled "Mineral Acid Leaching of Scandium from Bauxite Residue", presented by Prof. Dr. Maria Ochsenkuehn-Petropoulou in the 2nd International Bauxite Residue Valorization and Best Practices Conference-BR2018, which was held in Athens, Greece, 7-10 May 2018. The conference paper is available online at: http://svs2015-mtm.icts.kuleuven.be/indico/event/39/contribution/30 (accessed on 20 September 2018); The whole proceedings of the 2nd International Bauxite Residue Valorization and Best Practices Conference-BR2018, 7-10 May 2018, Athens, Greece are not available online and only a hard copy of them exists.

Abstract: Bauxite residue (BR) is a well promising resource for critical metals and especially scandium (Sc), a rare and expensive metal with increasing applications in advanced technology. Particularly, Greek BR's composition indicates a sound possibility for a commercially viable recovery of Sc under the conditions of an optimized leaching process and the subsequent use of advanced separation techniques. Leaching with mineral acids emerges as the dominant selection with comparison to other techniques. This study investigates an optimized leaching condition set on Sc recovery, using sulfuric acid as the most suitable among different acids tested, in the context of process economics and environmental constraints. Several variables were studied individually or combined in order to achieve high Sc concentration in the leachate as well as to ensure selectivity, especially in respect to iron. The most significant parameters proved to be the solid to liquid ratio (S/L), the final pH value as well as the use of recycling of leachate on fresh BR batches. The proposed process, using sulfuric acid at low acid molarities under ambient conditions was integrated rapidly leading to high and selective Sc recovery. A flow diagram of the developed leaching process in industrial scale was proposed based on continuous operation.

Keywords: bauxite residue; scandium; leaching; sulfuric acid

1. Introduction

Bauxite residue (BR), also called red mud, is the highly alkaline (pH>11) and very fine-grained slurry by-product after 'Bayer' process for alumina production. Its huge global annual production ~120million tones [1] has resulted in BR increasing accumulation, causing deposition problems and serious environmental impacts. The management and the safe disposal of this waste are therefore a major issue for bauxite and alumina industries affecting the production cost. The valorization of BR as a secondary raw material and as a metal resource of low cost could be a route for its reduction introducing the waste again in the economic cycle. BR is rich in minerals and metals of high economical interest. Its chemical composition depends directly on the origin of the bauxite ore and the conditions of Bayer process. It contains oxides and salts of the main elements Fe, Al, Ca, Na, Si, Ti and numerous trace elements such as V, Cr, Zn, Ga, Nb, Zr and Ta as well as rare earths - REEs (Sc, Y, lanthanides) [2].

In Greece "Aluminum of Greece" (AoG) produces annually about 750.000 tons of BR, which is characterized as chemically stable. Besides other metals, Greek BR is rich in REEs especially in scandium (Sc). It was found to contain ~1kg REEs/t of dry BR with a Sc content of ~120g/t of dry BR (0.02% Sc_2O_3) close to Sc main resources. Greek BR is enriched in REEs by a factor of two referring to the original bauxites, and the concentration of REEs is almost constant over about 25 years [2-5]. It is calculated that a full exploitation of Greek BR from AoG can produce about 1kt/yr of REEs oxides.

REEs and especially Sc are elements of high techno-economical interest because of their use in high-tech materials and modern applications. Scandium is exceptionally expensive especially in high purity with highly promising demand but low availability due to its few economically exploitable minerals and its difficult recovery from its deposits where it co-exists with radioactive elements [6].

European Commission's classification of Critical Raw Materials (CRMs) [7] ranks Sc as critically high on both supply risk and economic importance due to the decreasing available stockpiles combined with the globally limited production and the evolution of new applications [8-16]. The light-weight Al-Sc alloys with a content of 0.5-2% Sc find applications in the aerospace and defense technology and athletic equipment. Also, the use of Sc as electrolyte in solid oxide fuel cells thanks to its improved oxygen ion conductivity creates the conditions for a sustainable Sc supply route.

The economic value of REEs/t in Greek BR according to the recent target prices, shows that Sc corresponds to more than 90% of the total value, rendering its selective recovery attractive for industrial scale exploitation [17-20].

Hydrometallurgical treatment is the most commonly used technique for REEs including Sc, recovery from BR [21,22]. Several conventional mineral [3,4,17-29] and organic acids [3,28], as well as alkaline solvents (Na_2CO_3) [30] have been studied. The use of organic acids shows very low recovery yields while alkaline solvents hinder the following ion exchange and solvent extraction processes for Sc isolation and purification [14]. Other researchers [31-33] have tested ionic liquids in BR leaching and bioleaching but results fall short due to low Sc recovery yield, requirement for stronger conditions and the ionic liquids high cost. Under these drawbacks, the process viability in industrial scale seems quite uncertain. Concerning bioleaching and the requirement of specific microorganisms for the degradation of BR, there is still much research work to be done. In cases where BR pretreatment is applied prior to leaching such as the pyro-metallurgical roasting or smelting, the need of strong conditions and high energy consumption limits their economic performance [34,35].

The present work is a continuation of an over 20-year research in REEs recovery from BR that resulted to the development of an innovative method for the selective separation and purification of REEs and especially Sc, including nitric acid leaching, ion exchange, selective extraction-backstripping and HPLC processes [3-5,17-19,23-25,36,37]. The whole procedure has been performed in lab scale and partially scaled up to a pilot plant with comparable results [4,24,25].

In the present study, acidic leaching of BR using H_2SO_4 as leaching agent was investigated for scandium selective recovery. The selection of sulfuric acid was based on environmental and economic reasons as being of critical importance in industrial scale applications. Different variables such as acid molarity, solid to liquid ratio (S/L), leaching time, final pH, leaching temperature, kind of stirring, multistage leaching of the same BR with fresh acid and recycling of the leachate solution to fresh BR were tested and evaluated aiming at high Sc concentration and its selective recovery especially in respect to iron. The results reveal that the proposed process for Sc recovery is rather fast with scandium extraction being completed within less than 60 min, using low concentrations of sulfuric acid (<3M). The effects of S/L ratio, the adjustment of final pH, the multistage leaching and especially the recycling were proven to be critical achieving scandium recoveries up to 60% with low (<10%) iron impurities. Increasing the leaching temperature, the iron dissolution enhances resulting in reduced selectivity. The impact of the above parameters was evaluated in respect to Sc concentration in the leachate since this is the decisive factor for the implementation of any subsequent purification process ([**18**], §3.4.1). The results were compared to those obtained in previous studies with other mineral acids in lab and pilot plant scale. Sulfuric acid leads to a comparable Sc recovery and

Peer-reviewed version available at *Metals* **2018**, *8*, 915; doi:10.3390/met8110915

selectivity over iron, being more economically viable and environmentally friendly than the other investigated mineral acids.

2. Materials and Methods

All experiments were conducted using a BR (red mud) sample produced in December 2016, provided by AoG. The sample had a pH value of 11.3, and moisture content about 26%.

The sulfuric acid (H_2SO_4) used was of industrial grade 96-98% w/v (Kalogeropoulos S.A., Greece). A single standard Sc solution TraceCERT 92279 of 1000mg/L supplied by Fluka Chemie GmbH (Buchs, Switzerland) and a multi element standard solution IV for ICP CertiPUR 1.11355 of 1000mg/L for each element supplied by Merck KGaA (Darmstadt, Germany) were used for the preparation of working standard solutions.

Leaching experiments were performed adding appropriate amount of dry BR to 200-2000ml of 1-3M H_2SO_4 in order to result to 2-30% S/L ratios. For the leaching time effect study, a sample was collected at 5, 15, 30, 45 and 60 min.

For temperature experiments, 2M H_2SO_4 was preheated at 50 and 80^{o}C in conical flasks immersed in water baths on a magnetic stirrer hot plate. Appropriate amount of dry BR was added to the hot H_2SO_4 resulting to 10% S/L ratio and stirred for 60min. High temperature experiments were performed in an autoclave where 2M H_2SO_4 was added to dry BR resulted to 10% S/L ratio in the Teflon vessel. The vessel was introduced in the autoclave bomb and was heated at 160 and 230^{o}C (hot plate temperature) for 60min under magnetic stirring.

In all above cases, the final pH of the leachate was measured and the leachates were filtered under vacuum with 0.45μm cellulose nitrate membranes supplied by Whatman plc (part of GE Healthcare Life Sciences) (Little Chalfont, Buckinghamshire, UK) and stored for analysis.

Final pH adjustment of the leachate was performed by the addition of concentrated sulfuric acid to dry BR in order to achieve a final pH of the leachate about 0.1 – 0.2 and the mixture was allowed to be stirred up to 60min. pH and temperature were monitored by an electronic pH-meter (multi 350i, by WTW (Weilheim, Germany)). The leachates were filtered (0.45μm under vacuum) and stored for analysis.

For the multistage leaching experimental procedure an appropriate amount of dry BR was added to 1, 2, 3M H_2SO_4 in a conical flask resulting to S/L of 5 and 10%. The mixtures were stirred using a magnetic stirrer for 60min at ambient conditions. After leaching and centrifugation procedures, the precipitate was collected and re-treated with fresh H_2SO_4, while the supernatant liquid was removed, filtered (0.45μm under vacuum) and stored for analysis. The process was repeated thrice. The pH value of the leachate was measured after each repetition.

Finally, the leachate recycling experiments were conducted in a conical flask or sealed spherical flask by adding appropriate amount of dry BR in 1 and 2M H_2SO_4 resulting to S/L 10%. pH value was adjusted close to 0 with appropriate amount of concentrated H_2SO_4. After 60min of magnetic or mechanical agitation, the leachate was collected, filtered (0.45μm under vacuum) and reused on fresh BR sample. pH value was adjusted close to 0 with appropriate amount of concentrated H_2SO_4 prior each step. The process was repeated thrice including the first leaching.

Agitation effect was evaluated using the options of magnetic and mechanical stirring, with the latter to be optionally accompanied by bottom air feed and mild bubble-agitation.

All filtered PLS were analyzed for Sc (361.383nm) and main elements such as Fe (259.939 nm), Ti (334.940 nm), Si (251.611 nm) by ICP-OES Optima 7000DV, which was supplied by Perkin Elmer (Waltham, MA, USA). For the determination of all the elements, the calibration curve method was applied. pH measurements were carried out by the multi 350i pH-meter, with a SenTix® 41 precision electrode. A HeiTec magnetic stirring plate with heating and a mechanical stirrer Hei-Torque 100, both supplied by Heidolph (Schwabach, Germany), were used. High temperature experiments were performed in an autoclave bomb 4744 of 45ml capacity by Parr Instrument Company (Moline, IL, USA).

3. Results

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 3 October 2018 doi:10.20944/preprints201810.0063.v1

Peer-reviewed version available at *Metals* **2018**, *8*, 915; doi:10.3390/met8110915

Table 1 presents Sc and total REEs concentrations in different Greek BR lots from the AoG production, for an over 20-year period, revealing for Sc a small variation of about 11%. The initial concentration of Sc in this study's BR batches was estimated at 98.0±3.0 μg of Sc /g of BR after three replicates of lithium tetraborate fusion [4].

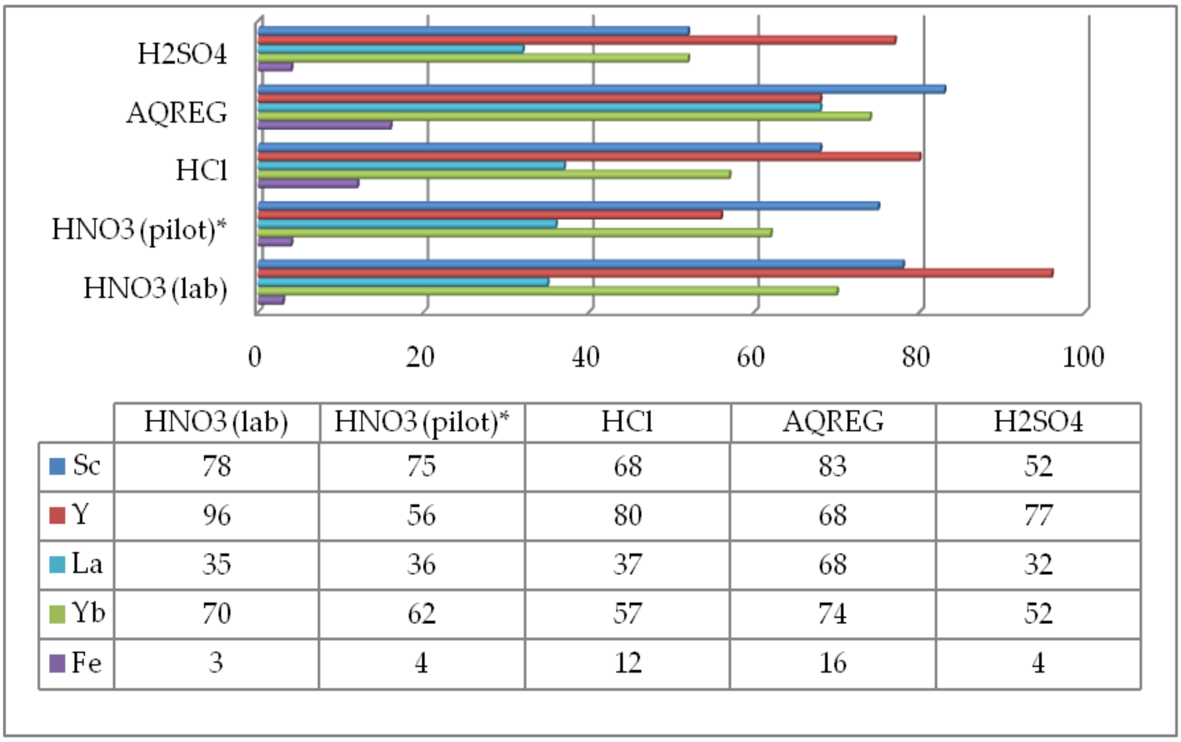
Table 1. Concentration [g/t] of Sc and REEs in Greek BR batches (1993-2016).

	BR 1993	**BR 2001**	**BR 2007**	**BR 2012**	**BR 2014**	**BR 2016**	**Mean**
Sc	127.9	107.0	130.0	110.0	104.7	98.0	112.9 ± 13.0
Total REEs	986.1	868.0	1010.5	1040.3	729.7	856.0	915.1 ± 118.2

3.1 Selection of leaching agent

Different mineral acids have been previously investigated as leaching agents in lab and pilot plant scale and the obtained results are presented in Fig. 1. As it is shown aqua regia (AQREG) gives the highest recovery for Sc and the other REEs, followed by nitric acid, hydrochloric acid, and sulfuric acid. However, the selectivity of the process shows the opposite trend. Co-extraction of iron and other main elements of BR hinder the subsequent processes of Sc isolation and purification. Sulfuric acid is preferred due to its selectivity, lower environmental impact as well as due to its significantly lower price -being even more than 50% of HNO_3 [38-44]. Leachability of other elements of techno-economical interest, such as Ga, Zr and Nb is also favored by sulfuric acid in comparison to nitric acid [18].

Optimization of leaching process is focused on Sc concentration rather than percent recovery, by taking into consideration the requirements of the consecutive separation process.



	HNO3 (lab)	HNO3 (pilot)*	HCl	AQREG	H2SO4
■ Sc	78	75	68	83	52
■ Y	96	56	80	68	77
■ La	35	36	37	68	32
■ Yb	70	62	57	74	52
■ Fe	3	4	12	16	4

**after two successive leaching steps*

Figure1. Recovery (%) of Sc and other REEs by leaching with different acids

Scandium recoveries obtained by lab scale and pilot plant experiments, carried out with HNO_3 are quite similar although a large scale process might require two leaching steps, due to the different dispersion conditions [17, 18, 24].

3.2 Effect of leaching time

The leaching reaction is fast and is practically completed within 60 min. Any increment of Sc recovery observed above 60 min is statistically insignificant. Almost 90% of the final Sc concentration can be achieved within 10 min under higher acid molarities (3M). A leaching time of 60 min was used for all experiments as adequate period for the completion of the reaction. The entire set of the relevant results is presented in Fig. 2.

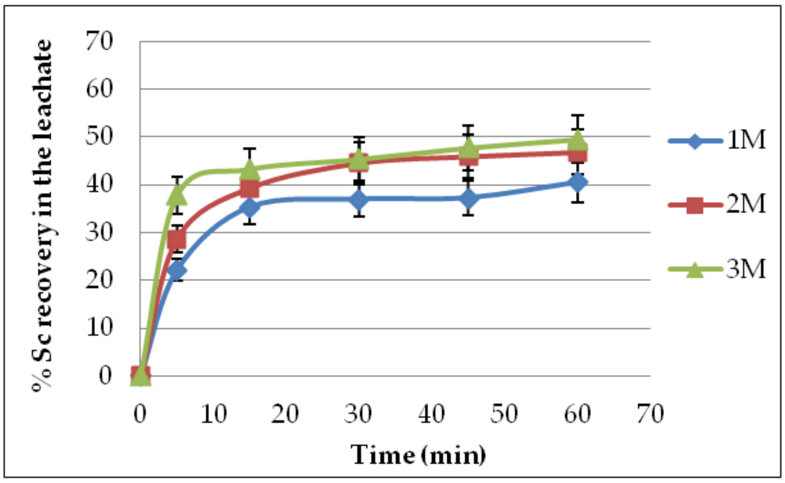
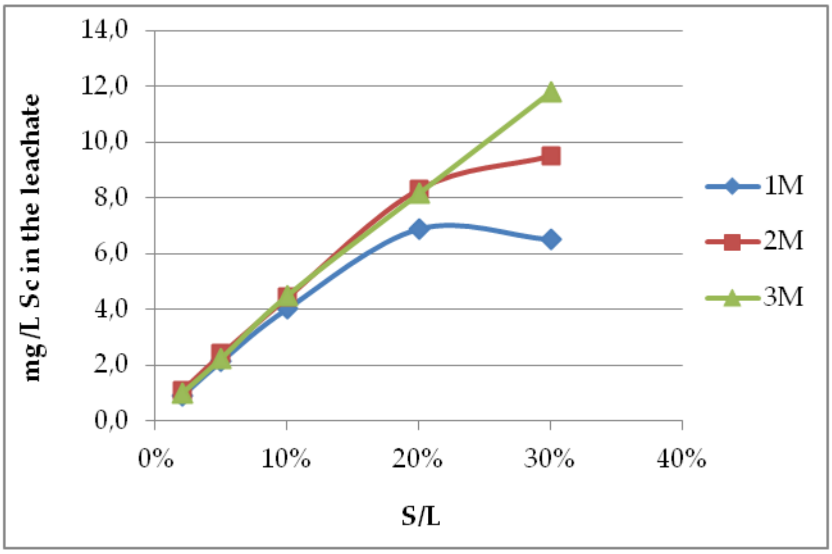


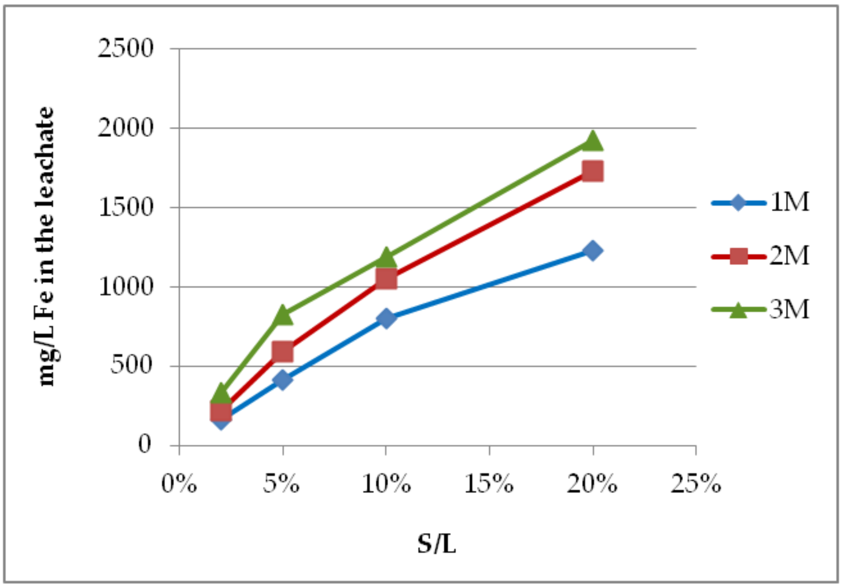
Figure 2. Leaching time effect for different acid molarities and S/L ratio 5% (1:20).

3.3 *Effect of acid molarity*

The effect of molarity depends on S/L ratio. Increasing molarity raises Sc concentration in the leachate as presented in Fig. 3a. The effect is significant for S/L ratios higher than 20%. The same results were also observed for iron (Fig. 3b). Acid molarities higher than 3M were also tested and although an enhanced Sc concentration appears, they are not proposed due to even higher iron dissolution and reduction of process selectivity. Lower molarities are more economically viable and environmentally friendly, as well as they ensure method selectivity. On the other hand, silica gel formation occurs when low acid molarities are combined with high S/L ratios. This is an important issue for hydrometallurgical processes under acidic conditions, when raw materials such as BR, have a Si content. Gel formation is caused due to the presence of silica in the solution as silicic acid (H_4SiO_4) at pH <7. The monomers connect to form polysilicic acid and colloids result to gel formation, as they entrap liquid inside their structure. The use of higher acid molarities >3M confront the problem even at high S/L ratios [45]. However, method's selectivity as well as environmental benefits on industrial scale up decline. Acid molarity of 2M was selected to compromise these contradictory effects.



(a)



(b)

Figure 3. Acid molarity effect on (a) Sc; (b) Fe concentration for different S/L ratios (2-20%) and 60 min leaching period.

3.4 Effect of S/L ratio

Sc recovery is decreased by S/L ratio increment especially at low acid molarities and high S/L ratio since the amount of the acid is not adequate for neutralizing BR and pH is not adjusted (Fig. 4). The essential outcome nevertheless concerns Sc concentration in the leachate. As presented in Fig. 3a, there is an almost linear correlation between S/L ratio and Sc concentration, for all acid molarities and ratios up to 20%. For ratios higher than 20%, acid molarity of at least 3M is required for sufficiently high Sc recovery in the leachate and avoidance of gel formation. Inefficiency of lower H_2SO_4 molarities to neutralize BR alkalinity at high S/L ratio results to high pH values, that do not favor the leaching efficiency (see §3.5). The higher values of S/L ratio induce a certain difficulty in handling of the leachate, due to silica gel formation. Since the key point is the leachate's Sc concentration rather than the percent recovery of Sc, higher S/L ratios at appropriate molarities are preferred. The use of 2M H_2SO_4 combined with S/L 20% seems a technically acceptable compromise.

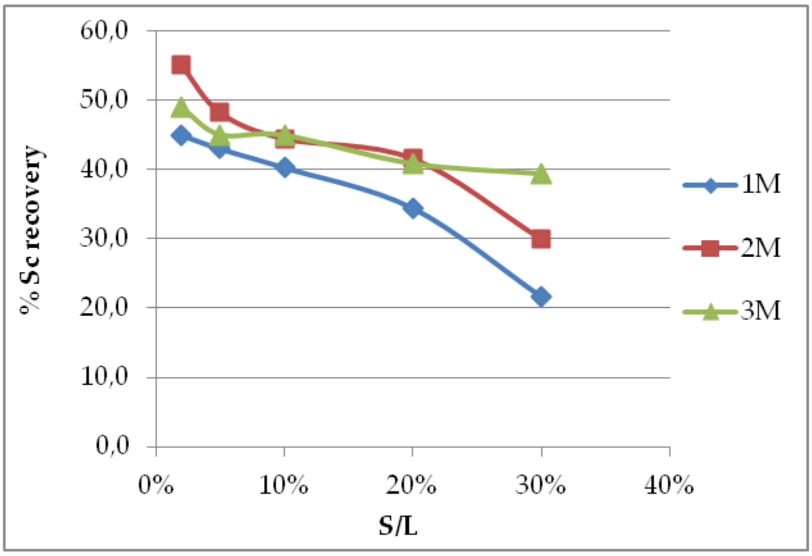


Figure 4. S/L effect on Sc % recovery at different molarities and 60 min leaching period.

3.5 Effect of pH adjustment

The final pH value of the leachate is a definite indicator of leaching process performance. A pH value close to 0.1 is related to significant improvement of Sc recovery, which is enhanced up to 25% in comparison to that at higher pH, especially in case of high S/L ratios. The set of the pertinent results is presented in Table 2. The optimum pH range has been found to be from 0.0 up to 0.2. Low pH values is therefore considered as mandatory for the increment of Sc concentration in the leachate. Furthermore, pH adjustment with addition of concentrated sulfuric acid during leaching reaction improves Sc recovery up to 6%, due to temperature synergy effect.

Table 2. pH values of the leachate for different S/L ratios and acid molarities - (t=60min)

S/L	M	final pH	% recovery
30%	1	2.00	21.2
30%	2	1.50	28.0
30%	3	0.32	40.0
20%	1	0.65	35.9
20%	2	0.28	42.5
20%	3	0.20	43.2
20%	pH adjusted*	0.082	49.2
10%	1	0.32	41.8
10%	2	0.16	44.7
10%	3	0.07	46.6
10%	pH adjusted*	0.11	52.0
5%	1	0.09	44.7
5%	2	0.01	49.0
5%	3	0.01	46.7

**pH adjustment at low values about 0.1 by the addition of concentrated 98% w/v H2SO4 during leaching reaction*

3.6 Temperature effect

Increased reaction temperature from 25 to 80°C at ambient conditions, and 160 and 230°C under autoclave conditions, improves only marginally the Sc recovery. Iron dissolution, on the other hand, is noticeably enhanced reaching a recovery of even 22% and a final concentration of 7g/L that diminishes method selectivity. The obtained results are presented in Fig. 5. The plotted iron recovery in the graph is multiplied by a factor of 2, for presentation reasons (it is marked as Fe*2).

Peer-reviewed version available at *Metals* **2018**, *8*, 915; doi:10.3390/met8110915

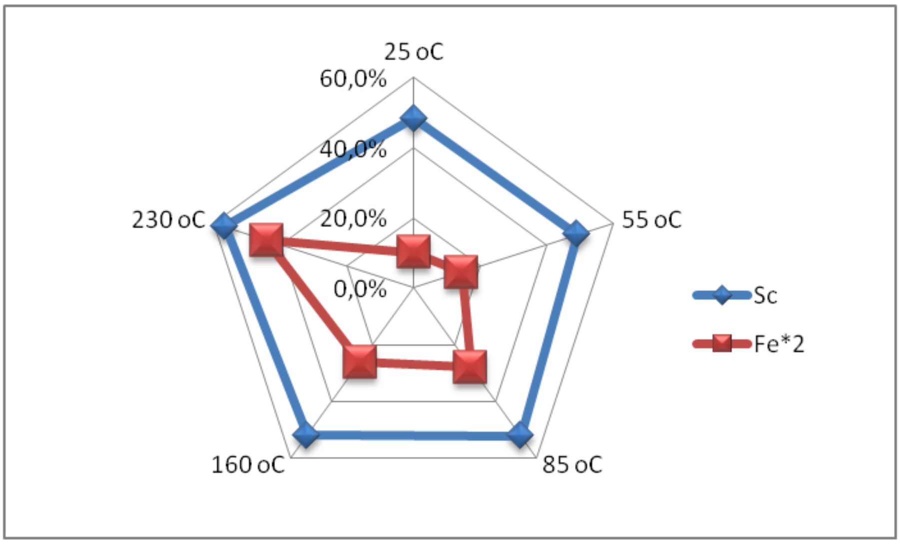


Figure 5. Effect of temperature on Sc and Fe recovery (S/L 10%, 2M H_2SO_4, t=60min).

Additional leaching experiments under extreme conditions were also performed, in order to assess the effect of high molarities (>3M) and high temperature combination. As expected, these experiments resulted to essential increment of Sc recovery (up to 70%) and concentration (about 20mg/L), with avoidance of gel formation, but with also almost complete dissolution of iron at the expense of selectivity. Such high Fe concentration in the leachate impedes any following ion exchange or solvent extraction processes for Sc separation and purification, due to similar ionic radii of Sc and Fe.

All above-mentioned variables (S/L, acid molarity, temperature, time) were also tested in respect to other main elements concentration, in order to satisfy the required specifications of feed solution for the subsequent purification process. As already pointed, Fe concentration is increased by temperature, S/L and molarity raising from 1040mg/L to 32500mg/L and Ti is increased with S/L ratio from 1430mg/L (for 20% S/L) to 6550mg/L (for 40% S/L). In contrast, the silicon concentration is suppressed at higher molarities (>3M) solving the silica gel formation problem. Ambient conditions show to be generally preferable, considering the Sc selectivity and the energy consumption cost, for an economically viable process design.

3.7 Effect of stirring mode

Three kinds of stirring were tested: magnetic stirring, mechanical agitation and mechanical with air bubbles agitation, with stirring speed at about 550-650rpm (see Fig. 6). As it is observed, the stirring mode has no effect on Sc recovery regardless the S/L ratios and acid molarities tested. These findings apply on lab scale experiments of this study. Larger scale setups might require more vigorous stirring conditions due to diverse dispersion mechanisms.

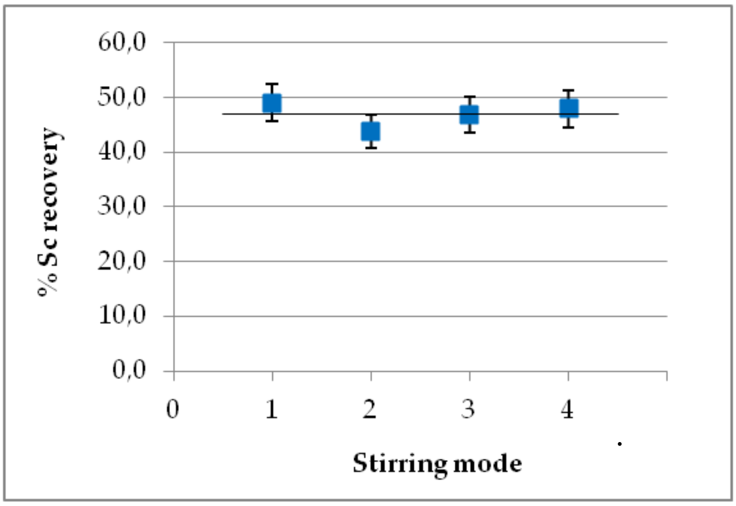
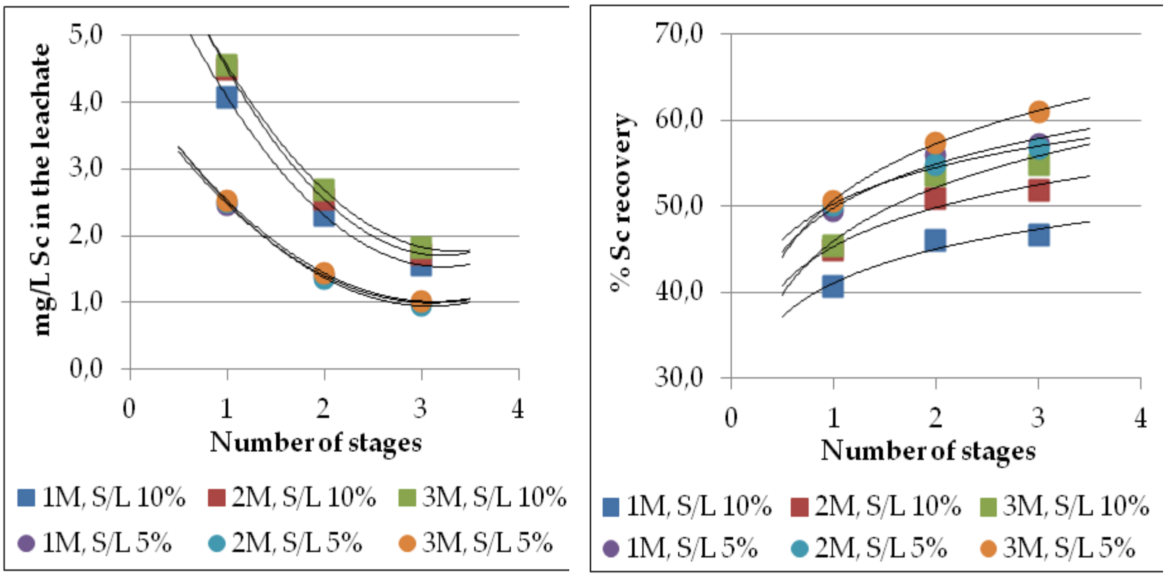


Figure 6. Effect of stirring mode (S/L 10%, 1M H_2SO_4, t=60min)
[1]Magnetic stirring 650rpm [2]Mechanical agitation 550rpm [3]Mechanical agitation 650rpm
[4] Mechanical agitation 550rpm with air

3.8 Effect of multi stage leaching process

Multi stage process refers to several successive leaching of the same bauxite residue sample with multiple fresh sulfuric acid batches. The entire process was performed in triplicates under ambient conditions for 60min. Different acid molarities and S/L ratios were studied and the results are presented in Fig.'s 7a&b. The multi stage leaching has positive effect on Sc recovery (Fig. 7b), while seriously reduces Sc concentration (Fig. 7a), due to the obvious increment of the final leachate volume by the multiple adding of fresh sulfuric acid batches. Regarding to iron extraction, it remains relatively low even after the third stage with a total recovery up to almost 10%. Despite the remarkable Sc recovery increase, multistage process is not advantageous for large scale applications, due to Sc concentration reduction and the large required volumes of acid feed.



(a) **(b)**

Figure 7. Multi stage effect on: (a) Sc concentration; (b) Sc % recovery for different acid molarities and S/L ratios (t=60min, ambient conditions).

Peer-reviewed version available at *Metals* **2018**, *8*, 915; doi:10.3390/met8110915

3.9 Effect of leachate recycling

Recycling process refers to multiple reusing (reflux) of the leachate on fresh bauxite residue samples. The target is threefold: a) the leachate enrichment in Sc with the lower possible impurities in main elements (mainly Fe and Ti), b) the enhancing of the leaching process economic viability, especially in industrial scale, and c) the simplifying of Sc further purification after leaching by ion exchange/extraction processes [15]. The whole process was performed at 3 sequential cycles using 1M and 2M acid molarities with additional pH adjustment close to zero, before each cycle. The obtained results for Sc (in μg/L), Ti and Fe (in mg/L) for both molarities are given in Fig. 8. As it is clearly illustrated, reusing of leachate solution thrice with combined pH adjustment results to almost tripled Sc concentration (~12000 μg/L). The correlation is linear with a R^2=1.0000 for 1M H_2SO_4 and 0.9997 for 2M H_2SO_4. Fe and Ti present also linear correlation with R^2=0.8712(1M)-0.9999(2M) and 0.9892(1M)-0.9987(2M) respectively. However, the final concentration remains at low acceptable levels for Fe and Ti. The maximum measured Fe concentration (3 cycles 2M H_2SO_4) is 3000mg/L corresponding to ~10% recovery. Recycling of 1.5 times, which is possible in continuous operation in industrial scale (see Fig.11) satisfies the required PLS specifications for subsequent ion exchange process such as Sc >6mg/L, Fe <30000mg/L and Ti <1700mg/L [15]. Additionally, leachate recycling achieves lower acid and water consumption, promoting the viability of a large scale application while also getting the whole process more environmentally friendly.

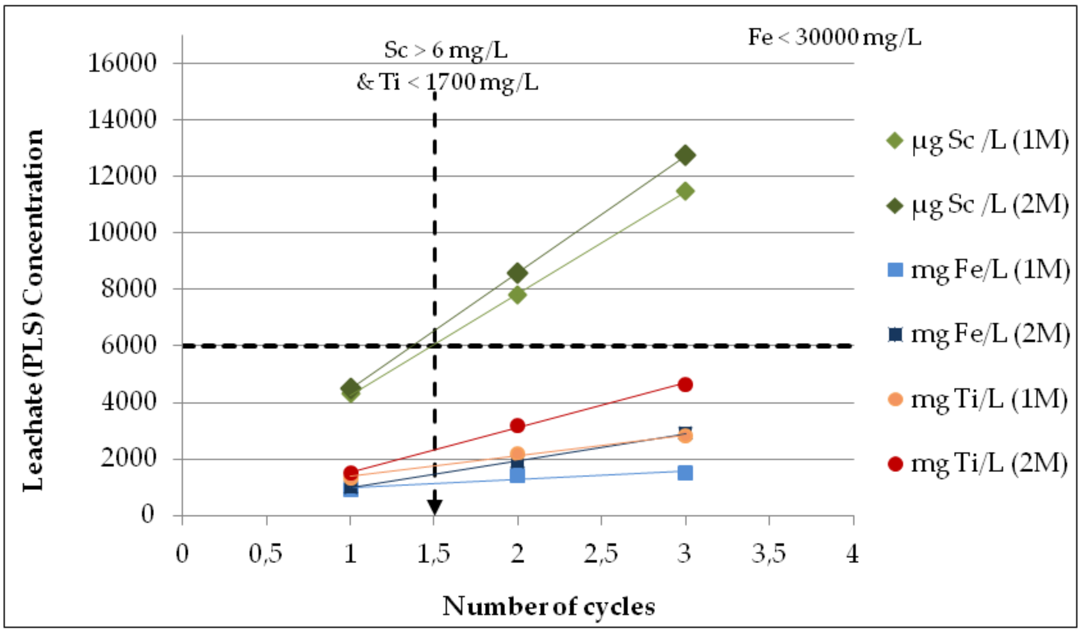


Figure 8. Leachate recycling with pH adjustment (S/L 10%, 1 and 2M H_2SO_4, pH≈0, t=60min, ambient conditions).

3.10 Statistical evaluation

Method reproducibility was evaluated by comparing the results from various leaching experiments, keeping the same research team and analytical technique, as well as the same raw material and leaching conditions. The variation of leaching efficiency is presented in Fig. 9. The average is 42.3% with a standard deviation ±2.8%.

Peer-reviewed version available at *Metals* **2018**, *8*, 915; doi:10.3390/met8110915

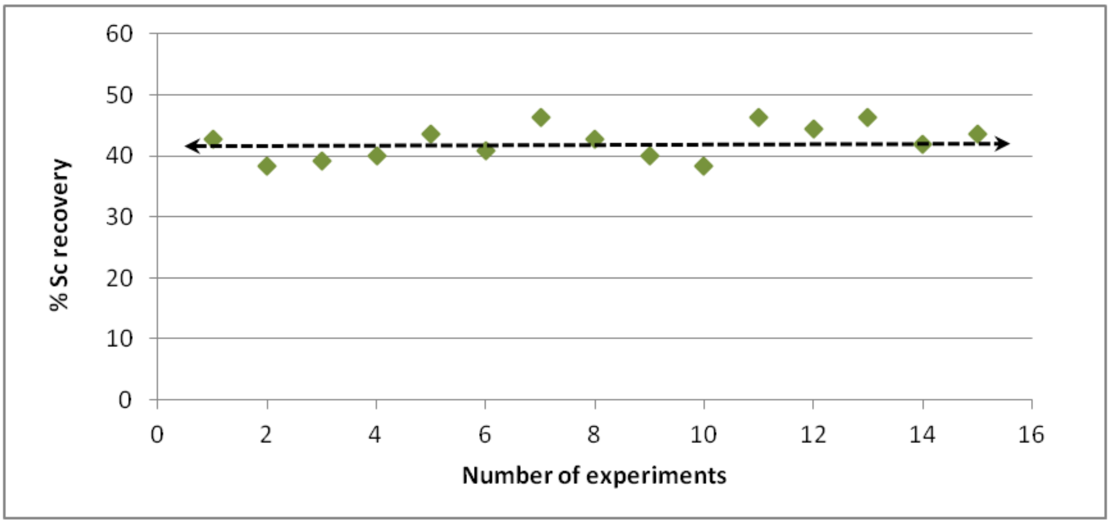


Figure 9. Reproducibility of leaching process (S/L 5%, 1M H_2SO_4, t=60min)

One-way ANOVA statistical analysis was applied to the experimental data in order to evaluate the contribution of each investigated parameter on Sc recovery and concentration in the leachate solution. The three independent parameters introduced were time, S/L ratio and molarity, while the two dependent variables were percent recovery and concentration. Solid to Liquid ratio (S/L) has been proved to contribute mostly to Sc concentration, while leaching time is more critical for Sc recovery [18].

Two dimension projection of two parameters interaction (S/L ratio and time) on Sc concentration in the leachate solution is presented in Fig. 10. As shown, the maximum Sc concentration is achieved at high S/L ratio and long leaching duration.

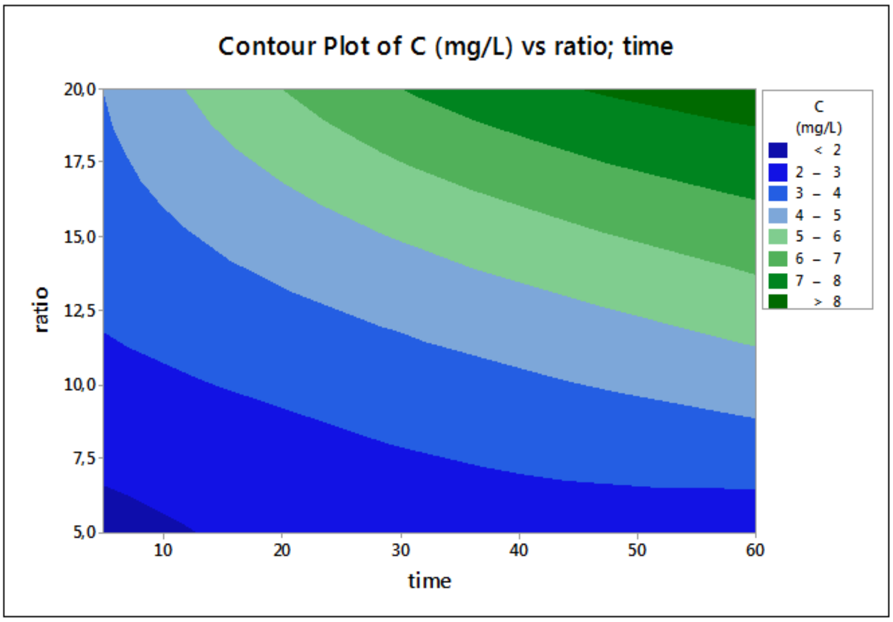


Figure 10. Two-factor (S/L ratio and leaching time) interaction, 2D projection on the extracted Sc concentration in the leachate.

4. Assessment and Conclusions

BR leaching using H_2SO_4 for the recovery of Sc at ambient conditions is a rapid process, which is practically integrated within 60 min. Final pH of the solution is critical and it demands pH adjustment in the range of 0.0 to 0.2. The proposed acid molarity is 2M, as a result of a technical compromise between the needed higher values for the avoidance of the Si-caused gel formation, and the lower values that ensure Sc selectivity, mainly with respect to Fe. Solid to Liquid ratio (S/L), as well as leachate solution reusing are crucial for Sc concentration. A minimum of 10% slurry concentration (S/L ratio) and two cycles of leachate reusing are suggested. Elevated temperature is not proposed due to high Fe dissolution at the expense to the Sc selectivity, while a multi-stage process reduces Sc concentration despite the raise of its recovery. The criteria for the parameters selection involve environmental and process economics aspects, as well as compliance with the requirements of the consecutive Sc separation process.

Future application of the developed leaching process in industrial scale can be based on the conceptual design for a continuous process, which is presented in the flow diagram of Fig.11.

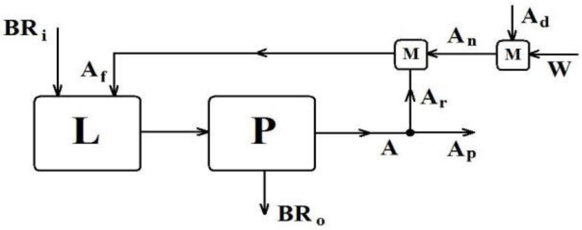


Figure 11. Conceptual design for a continuous BR leaching process.

where:

- L= Leaching reactor. Indicative type: CF-CSTR (*Continuous Flow-Continuous Stirred Tank Reactor*), with a heating/cooling mantle to be an option.
- P= Unit for Purification of leachate from solids. Indicative configuration: Intermediate Tank, Filter Press, or Flocculator/Filters, and PLS Tank.
- M= Mixing unit. Indicative configuration: Continuous flow mixing device, with a heat dissipation system.
- BR= Bauxite Residue streams with moisture content.
  Subscripts: i = input (alkaline solids stream), o = output (acidic solids stream).
- A= Acid streams (sulfuric acid solutions).
  Subscripts: f= leaching feed, p= product (PLS), n= new (fresh solution), r= recycling PLS, d= dense acid (93-98% w/w). (Reflux ratio) = (Number of cycles in batch processing) – 1.
- W= Water stream; mixture of raw water with used water from Filter Press cleaning.

Acknowledgments: The research leading to these results has been performed within the SCALE project and received funding from the European Community's Horizon 2020 Program (H2020/2014-2020), under Grant Agreement no. 730105. The companies II-VI Inc. (Saxonburg, PA, USA) and MYTILINEOS S.A. former Aluminum of Greece S.A. (AoG) are also gratefully acknowledged for the fruitful collaboration and cooperation in the context of Scale, as well as in previous joint projects.

Author Contributions: This work has been performed by the members of Laboratory of Inorganic and Analytical Chemistry of Department of Chemical Sciences (M. O.-P.; L.-A. T., Th. L., K.-M. O, C. S., O.S. and F. T.) in collaboration with the Department of Process Analysis and Plant Design (K. H.; P. G.) of NTUA School of Chemical Engineering. L.-A. T., Th. L., C. S. and O.S. performed the experiments; Th. L. and L.-A. T. integrated ICP-OES measurements; L.-A. T. and Th. L. evaluated the data and wrote the draft paper; M. O.-P supervised the whole work and corrected the draft paper; K. S. designed the proposed continuous process for the future industrial scale up; K.-M. O., P.G and F.T. reviewed the paper.

Conflicts of Interest: The authors declare no conflict of interest. The results of this work have been derived in the context of the SCALE project (Grant Agreement No. 730105) and the publication is in accordance with its terms. The funding sponsors (EU/EASME) had no role in the design of the study, in the collection, analyses, or interpretation of data, and in the writing of the manuscript.

References

1. Power, G.; Grafe, M.; Klauber, C. Bauxite residue issues: I. Current management, disposal and storage practices. *Hydrometallurgy* **2011**, 108, 33-45, https://doi.org/10.1016/j.hydromet.2011.02.006
2. Ochsenkühn-Petropoulou, M.; Lyberopulu, Th.; Parissakis, G. Direct determination of lanthanides yttrium and scandium in bauxites and red mud from alumina production. *Anal. Chim. Acta* **1994**, 296 (3) 305-313, https://doi.org/10.1016/0003-2670(94)80250-5
3. Lyberopulu, Th. Determination and Recovery of Rare Earths from Bauxites and Red Mud. PhD Thesis, National Technical University of Athens, Athens, Greece, 1996. Available online: https://www.didaktorika.gr/eadd/handle/10442/8817 (accessed on September 2018)
4. Tsakanika, L.-A. Separation and recovery of lanthanides from red mud by use of selective extraction and chromatographic techniques. PhD Thesis, National Technical University of Athens, Athens, Greece, 2013.
5. Ochsenkühn-Petropoulou, M.; Tsakanika, L.-A.; Lymperopoulou, Th. Process control of an innovative method for the recovery and separation of rare earths from red mud by different analytical techniques. Proceeding of 1st European Rare Earth Resources Conference (ERES 2014), Milos Island, Greece, 4-7 September 2014, 28-29.
6. Scandium Investing. Why Scandium Could Be a Huge Opportunity: Commercially Viable Scandium Deposits Are Rare, but There Is Indeed Opportunity in this Market. Investing News Network. 12 April 2017. Available online: http://investingnews.com/daily/resource-investing/critical-metals-investing/scandiuminvesting/scandium-production-the-problem-and-the-opportunity/ (accessed on 20 September 2018).
7. European Commission: Critical Raw Materials. Third List of Critical Raw Materials for the EU of 2017. Available online: https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en (accessed on 20 September 2018).
8. Gambogi, J.; U.S. Geological Survey. Mineral Commodity Summaries, SCANDIUM. January 2017. Available online: https://minerals.usgs.gov/minerals/pubs/commodity/scandium/mcs-2017-scand.pdf (accessed on 20 September 2018).
9. Røyset, J.; Ryum, N. Scandium in aluminium alloys. *Int. Mater. Rev.* **2005**, 50, 19–44, https://doi.org/10.1179/174328005X14311
10. Hildeman, G.; Koldenhoven, K. Mechanical Properties and Applications of Aluminum Scandium Alloys at Elevated Temperatures. *Light Metals* **2018**, 1581-1587, https://doi.org/10.1007/978-3-319-72284-9_206
11. Schmidtke, K.; Palma, F.; Hawkins, A.; Emmelmann, C. Process and mechanical properties: Applicability of a scandium modified al-alloy for laser additive manufacturing. *Phys. Procedia* **2011**, 12, 369–374, https://doi.org/10.1016/j.phpro.2011.03.047
12. Pan, F.; Liu, T.; Zhang, X.; Tang. A.; Wang, W. Effects of scandium addition on microstructure and mechanical properties of ZK60 alloy. *Materials International* **2011**, 21, 59−65 https://doi.org/10.1016/S1002-0071(12)60026-4
13. Duyvesteyn, W.P.C.; Putnam, G.F. EMC Metals Corporation, White Paper. SCANDIUM: A Review of the Element, Its Characteristics, and Current and Emerging Commercial Applications. May 2014. Available online: http://www.scandiummining.com/i/pdf/Scandium-White-PaperEMC-Website-June-2014-.pdf (accessed on 20 September 2018).
14. UC RUSAL Sustainability Report 2016. Scientific and Technological Development. Available online: https://sr.rusal.com/company-management-system/scientific-and-technical-development.php (accessed on 23 January 2018).
15. Project SCALE: Production of Scandium Compounds and Scandium Aluminum Alloys from European Metallurgical by-Products. European Community's Horizon 2020 Programme. Available online: http://cordis.europa.eu/project/rcn/206331_en.html (accessed on 20 September 2018).
16. Awd, M.; Tenkamp, J.; Hirtler, M.; Siddique, S.H.; Bambach, M.;Walther, F. Comparison of microstructure and mechanical properties of scalmalloy® produced by selective laser melting and laser metal deposition. *Materials* **2018**, 11, 17, https://doi.org/10.3390/ma11010017
17. Lymperopoulou, Th.; Tsakanika, L.A.; Ochsenkühn, K.M.; Ochsenkühn-Petropoulou, M. Optimization of Mineral Acids Leaching Process for the Recovery of Rare Earth Elements from Greek Red Mud. Proceedings of 2nd conference on European Rare Earth Resources (ERES2017), Santorini Island, Greece, 28-31 May 2017, 182-184 Available on line: https://www.dropbox.com/sh/h1m9r8woixspd3f/AABzcTZ1UXs1Ex9j0kzeleODa/ABSTRACTS/VIA/VIA1.pdf?dl=0 (accessed on 20 September 2018).

18. Ochsenkuehn-Petropoulou, M.; Lymperopoulou, Th.; Tsakanika, L.A.; Ochsenkuehn, K.M.; Hatzilyberis, K.; Georgiou, P.; Stergiopoulos, Chr.; Tsopelas, F. Mineral Acid Leaching of Scandium from Bauxite Residue. Proceedings of 2nd International Bauxite Residue Valorization and Best Practices Conference (BR2018), Athens, Greece, 7-10 May 2018, 373-379, Available online: http://svs2015-mtm.icts.kuleuven.be/indico/event/39/contribution/30 (accessed 20 September 2018).
19. Hatzilyberis, K.; Lymperopoulou, Th.; Tsakanika, L.-A.; K.-M. Ochsenkühn, Georgiou, P.; Defteraios, N.; Tsopelas, F.; Ochsenkühn-Petropoulou, M.; Process Design Aspects for Scandium-Selective Leaching of Bauxite Residue with Mineral Acids. *Minerals* **2018**, 8, 79, https://doi.org/10.3390/min8030079
20. Mineral Prices, Rare Earth Metals. Available online: http://mineralprices.com/default.aspx#rar (accessed on 16 September 2018).
21. Liu, Z.; Li, H. Metallurgical process for valuable elements recovery from red mud—A review. *Hydrometallurgy* **2015**, 155, 29-43, https://doi.org/10.1016/j.hydromet.2015.03.018
22. Wang, W.; Pranolo, Y.; Cheng, Ch. Y. Metallurgical processes for scandium recovery from various resources: A review. *Hydrometallurgy* **2011**, 108, 100-108, https://doi.org/10.1016/j.hydromet.2011.03.001
23. Ochsenkühn-Petropulu, M.; Lyberopulu, Th.; Ochsenkühn, K.M.; Parissakis, G. Recovery of lanthanides and yttrium from red mud by selective leaching. *Anal.Chim.Acta,* **1996**, 319, 249-254, https://doi.org/10.1016/0003-2670(95)00486-6
24. Ochsenkühn-Petropoulou, M. Implementation and demonstration in pilot unit of a new processing method and use of red sludge, residue of metallurgical process of Greek Industry (EPET II/research program), Final Report, In M. Ochsenkühn-Petropoulou (Ed.), Laboratory of Inorganic and Analytical Chemistry, School of Chemical Engineering NTUA and Aluminium of Greece S.A., Athens, Greece, 2001.
25. Ochsenkühn-Petropoulou, M.; Hatzilyberis, K.; Mendrinos, L.; Salmas, C. Pilot Plant Investigation of the Leaching Process for the Recovery of Scandium from Red Mud, *Ind. Eng. Chem. Res.* **2002**, 41 5794-5801, https://pubs.acs.org/doi/abs/10.1021/ie011047b
26. Jha, M. K.; Kumari, A.; Panda, R.; Kumar, J. R.; Yoo, K.; Lee, J. Y. Review on hydrometallurgical recovery of rare earth metals. *Hydrometallurgy* **2016**, 165, 2-26, https://doi.org/10.1016/j.hydromet.2016.01.035
27. Yagmurlu, B.; Dittrich, C.; Friedrich, B. Effect of aqueous media on the recovery of scandium by selective precipitation. *Metals* **2018**, 8, 314, https://doi.org/10.3390/met8050314
28. Borra C. R.; Pontikes Y.; Binnemans K.; Van Gerven T. Leaching of rare earths from bauxite residue (red mud). *Minerals Engineering* **2015**, 76, 20-27, https://doi.org/10.1016/j.mineng.2015.01.005
29. Ujaczki, É.; Zimmermann, Y. S.; Gasser, C. A.; Molnár, M.; Feigl, V.; Lenz, M. Red mud as secondary source for critical raw materials – extraction study. *J Chem Technol Biotechnol* **2017**, 92, 2835–2844, https://doi.org/10.1002/jctb.5300
30. Petrakova, OV; Panov, AV; Gorbachev, SN; Klimentenok, GN; Perestoronin, AV; Vishnyakov, SE; Anashkin, VS; Improved efficiency of red mud processing through scandium oxide recovery. In: Hyland M (ed) *Light Metals* **2015**, Wiley, New York, 91–96, https://doi.org/10.1007/978-3-319-48248-4_17
31. Bonomi, Ch.; Giannopoulou, I.; Panias, D. Correlation of scandium and titanium during leaching of bauxite residue (red mud) by an imidazolium ionic liquid. Proceedings of 2nd conference on European Rare Earth Resources (ERES2017), Santorini Island, Greece, 28-31 May 2017. Available on line: https://www.researchgate.net/publication/321162111_CORRELATION_OF_SCANDIUM_AND_TITANIUM_DURING_LEACHING_OF_BAUXITE_RESIDUE_RED_MUD_BY_AN_IMIDAZOLIUM_IONIC_LIQUID (accessed 16 September 2018).
32. Davris, P.; Balomenos, E.; Panias, D.; Paspaliaris, I. Selective leaching of rare earth elements from bauxite residue (red mud), using a functionalized hydrophobic ionic liquid. *Hydrometallurgy* **2016**, 164, 125-135, https://doi.org/10.1016/j.hydromet.2016.06.012
33. Qu, Y; Lian, B; Bioleaching of rare earth and radioactive elements from red mud using Penicillium tricolor RM-10. *Bioresour Technol* **2013**, 136, 16–23, https://doi.org/10.1016/j.biortech.2013.03.070
34. Borra, CR; Mermans, J; Blanpain, B; Pontikes, Y; Binnemans, K; Van Gerven, T; Selective recovery of rare earths from bauxite residue by combination of sulfation, roasting and leaching. *Miner Eng* **2016**, 92, 151–159, https://doi.org/10.1016/j.mineng.2016.03.002
35. Borra, CR; Blanpain, B; Pontikes, Y; Binnemans, K; Van Gerven, T; Smelting of bauxite residue (red mud) in view of iron and selective rare earths recovery. *J Sustain Metall* **2015**, 2, 28–37. https://doi.org/10.1007/s40831-015-0026-4

36. Tsakanika, L.; Ochsenkühn-Petropoulou, M.; Mendrinos. L. Investigation of the separation of Rare Earth elements from red mud by use of reversed-phase HPLC. *Anal. Bioanal. Chem* **2004**, 379, 796-802, https://doi.org/10.1007/s00216-004-2667-1
37. Tsakanika, L.-A.; Ochsenkühn-Petropoulou, M. Separation and recovery of rare earths after red mud leaching by cation - exchange chromatography. Proceedings of International Bauxite Residue Valorization and Best Practices Conference (BR2015), Leuven, Belgium, 5-7 October 2015, 309-315. Available online: http://conference2015.redmud.org/wp-content/uploads/2015/10/Lamprini-Areti-TSAKANIKA-secure.pdf (accessed on 16 September 2018).
38. http://www.sunsirs.com/uk/sectors-14.html (accessed on 23 September 2018).
39. http://www.sunsirs.com/uk/prodetail-236.html (accessed on 23 September 2018).
40. http://www.sunsirs.com/uk/prodetail-723.html (accessed on 23 September 2018).
41. www.alibaba.com/product-detail/industrial-Sulfuric-Acid-Price-H2SO4-98-_2014682840.html?spm=a2700.7724857.normalList.26.466915ebpsz89c (accessed on 23 September 2018).
42. www.alibaba.com/product-detail/Industrial-Grade-HNO3-Liquid-Nitric-Acid_60771810678.html?spm=a2700.7724857.normalList.38.3eca7bb4Ibng1A (accessed on 23 September 2018).
43. https://www.kemcore.com/catalogsearch/result/?q=sulphuric+acid (accessed on 23 September 2018).
44. https://www.kemcore.com/catalogsearch/result/?q=nitric+acid+68%25 (accessed on 23 September 2018).
45. Alkan, G; Yagmurlu, B; Cakmakoglu, S; Hertel, T; Kaya, Ş; Gronen, L; Stopic, S; Friedrich, B; Novel Approach for Enhanced Scandium and Titanium Leaching Efficiency from Bauxite Residue with Suppressed Silica Gel Formation, *Scientific Reports* **2018**, 8, 5676, https://doi.org/10.1038/s41598-018-24077-9