

METALS SPECIATION IN BAUXITE RESIDUE WITH IMPLICATIONS TO ITS USE AS AN IMMOBILISATION AGENT

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Abstract

Sequential extraction was applied for the characterisation of the raw Bauxite residue (BBR) from Bosnia and Herzegovina and the sample with sorbed Ni(II) ions (BBR-Ni). Five operationally defined fractions of Fe, Al, Mn, Ni, Pb, As, Cd, Cr, Cu and Zn were separated: exchangeable (F1), bound to carbonate (F2), bound to Fe,Mn-oxides (F3), bound to the organic matter (F4) and residual (F5). Investigated elements were primarily found in F5 and F3 fractions. Considering the content of elements in the most labile fraction F1, only small concentration of Cr was detected. Al in F2 may pose an environmental risk, due to its high total content. Generally, results indicate low mobility of investigated elements contained in BBR, low mobility of Ni(II) in spent BBR form, and encourage further studies of BR as an immobilisation agent.

Introduction

One of the methods for the purification of contaminated water and remediation of polluted soil is based on the utilisation of inorganic sorbents/ion-exchangers, with high capacity, chemical stability and low cost.^{1,2,3} In this regard, applicability of natural minerals (zeolite, clay, oxides) is well known. However, aiming at sustainable development, practical feasibility of various industrial wastes having appropriate chemical composition needs to be considered. The potential use of wastes as immobilisation matrixes for heavy metals, metalloids and radionuclides from polluted water and soil was addressed in many studies.^{2,4} Materials such as fly ash, blast furnace sludge, waste slurry, iron (III) hydroxide, bauxite residue, etc., are largely available and economical, display high sorption capacities, and at the same time, their utilisation saves the consumption of the conventional natural sorbents. Due to the heterogeneous mineral composition, Bauxite Residue (BR) is one of the

industrial wastes with promising sorption properties.^{5,6,7} BR occurs in huge quantities during alumina production, and exhibits complex and variable characteristics.⁵ Although being classified as a non-hazardous waste, its disposal in the landfills present an environmental risk, mainly due to small size of mineral particles, high pH and excessive amounts.^{8,9} What's more, elevated concentrations of certain toxic elements and/or radioactivity can pose a threat to the environment, wildlife and human health.^{5,10,11} A huge need to reduce the burden on the environment caused by BR accumulation can be accomplished by finding ways for useful applications, accompanied by the analysis of the risk.

To assess the environmental impact of BR, and to explore the safety of its use as an immobilisation agent, information on the leachability of certain elements contained in RM is vital. In addition, the stability of sorbed metals is important information for management of spent BR (regeneration and/or disposal options). In this regard, determination of metal speciation gives more information about the potential release, migration and toxicity of pollutants than their total concentrations. Heavy metals and metalloids are bound by a variety of mechanisms to different BR minerals and the quantification can be done using chemical solutions of varying compositions and ability to release metals from the different pools. In this study, sequential extraction protocol was applied for the analysis of the overall content and the mobility of various elements in raw BR sample from Bosnia and Herzegovina, and in the sample with sorbed Ni(II) ions.

Materials and Methods

Samples preparation

The sample of red mud was taken from "Alumina" Factory (Bosnia and Herzegovina). Solid phase was separated from alkaline solution by decanting and drying at room temperature (20 ± 2 °C). After grinding and homogenisation of dry residue, sample BBR was obtained. Ni²⁺-loaded sample (BBR-Ni) was prepared by equilibrating 20 ml of Ni(NO₃)₂ solution (30 mg/l) with 1.000 g of BBR, in 50 mL centrifuge tube, on the overhead shaker (10 rpm) for 24 h. Solid/liquid separation was achieved by centrifugation at 7000 rpm for 15 min. The solid residues were rinsed with 10 mL of Milli-Q water, followed by centrifugation and drying.

Sequential extraction

Prepared samples were subjected to sequential extraction, following a modified Tessier procedure.¹² Starting from 1.000 g of sample, selected elements were partitioned into five operationally defined fractions: F1 - exchangeable (with 8 ml of 1 M MgCl₂ (pH = 7.0) at room temperature for 1 h with continuous agitation); F2 -

bound to carbonates (residue from previous step + 8 ml of 1 M NaOAc, pH = 5, adjusted with HOAc, at room temperature for 5 h with continuous agitation); F3 - bound to iron and manganese oxides (residue from previous step + 20 ml of 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25 % (v/v) HOAc for 6 h at 96 ± 3 °C with occasional agitation); F4 - bound to organic matter (residue from previous step + 3 ml of 0.02 M HNO_3 and 5 ml of 30 % H_2O_2 , pH = 2, adjusted with HNO_3 , for 2 h at 85 ± 2 °C with occasional agitation and second 3 ml aliquot of 30 % H_2O_2 , pH = 2, adjusted with HNO_3 was then added and the sample was heated for 3 h at 85 ± 2 °C with intermittent agitation. After cooling, 5 ml of 3.2 M NH_4OAc in 20 % (v/v) HNO_3 was added and the sample was diluted to 20 ml followed by continuous agitation at room temperature for 30 min); F5 - residual (residue from previous step with 50 mL of 6 M HCl for 9 h at 85 ± 2 °C). Compared to the original method, alternative conditions for F5 phase extraction were adopted.¹³

Prior to concentration measurements, extraction solutions were filtered using 0.45 μm pore size Millipore syringe filters. Extractions of BBR and BBR-Ni samples were performed in duplicate. The concentrations of elements were determined using ICP-OES (Inductively coupled plasma atomic emission spectrometer) iCAP 6500 Duo (Thermo Scientific, United Kingdom), equipped with the solid state RF generator and RACID86 Charge Injection Detector (CID) detector. Determination was done using external calibration with standards prepared from single stock solutions of 1000 ppm (Merck, Germany). Stock solutions were mixed into multi-standard working solutions according to their concentrations in BBR sample. Working standard solutions were matrix matched according to each extraction solution which was applied.

Results and Discussion

Overall content of selected elements in BBR

Analysis of BBR showed that it was composed of Fe_2O_3 (42.42 %), Al_2O_3 (18.08 %), SiO_2 (12.62 %), TiO_2 (4.64 %), CaO (2.86 %), Na_2O (8.92 %), loss of ignition was 7.93 %, and pH (at 1:1 solid/water ratio) was 10.6.¹⁴

The results of BBR sequential extraction are presented in Table 1 and Figure 2. Pseudo-total amounts of contained elements are calculated as the sum of metals from all five fractions. In agreement with BBR chemical and mineralogical studies,¹⁴ Fe and Al were the most abundant. Overall content of other investigated elements varied within wide limits (from 0.250 to 3850 $\mu\text{g/g}$), with the following decreasing trend: $\text{Mn} > \text{Ni} > \text{Cr} > \text{Zn} > \text{Pb} > \text{As} > \text{Cu} > \text{Cd}$. The content of elements in the BBR was in the range of values published for other samples (Table 1), except for the Mn and Ni

which were higher. From Table 1, the diversity of BR chemical compositions can be observed, however, it is noticeable that concentrations of Cd and Cu were commonly low in all investigated samples, whereas Mn and Cr were present in high amounts.

Table 1: Pseudo-total amounts of selected elements in BBR and some other BR samples

Element	BBR, Alumina (BiH, this study)	Alcoa (Spain) ¹⁰	Ajka (Hungary) ¹¹	Kidričevo (Slovenia) ¹¹
Fe (mg/g)	550±40	261±2	560±30	380±20
Al (mg/g)	106±6	65.7±5.7	200±10	220±10
Mn (µg/g)	3850±160	406±20	1180±60	367±18
Cr (µg/g)	580±10	1350±102	1120±60	450±20
Ni (µg/g)	820±30	80±3	375±20	51±3
Zn (µg/g)	300±10	80±4	n.a.	n.a.
Pb (µg/g)	230±15	50±8	230±10	73±4
As (µg/g)	75±4	1.0±0.1	213±11	53±3
Cu (µg/g)	61±3	52±3	71±4	30±2
Cd (µg/g)	0.250±0.017	1.3±0.1	3.0±0.2	1.00±0.05

Distribution of selected elements in BBR and BBR-Ni

Giving that only a fraction of examined elements is labile and potentially bioavailable, the results of sequential extraction provide insight into their mobility and toxicity. The content of toxic elements in phase F1 is the most critical, since these fractions can be easily released into the environment. The pollutants accumulated in F2 are also potentially dangerous, as their mobility increases in acidic environment. Mobility of elements further decreases from F3 to F5 phase, as well as the associated risks.

The largest proportions of all investigated elements were found in F5 (Figure 1). Considering macro-elements, Fe was almost exclusively in residual phase (99.87%), while Al was distributed largely between F5 (61.35 %), F3 (23.50 %) and F2 (11.47 %). Content of heavy metals and As in F5 was in the range 67.72-98.79%, with lesser amounts in F3 (0.17-22.62 %) and in F2 (0.14-8.66 %). Mobility of Cd was somewhat higher in respect to other elements, nevertheless, its overall concentration was insignificant. In general, the concentrations of investigated elements in F1 were negligible, except for Cr (0.08 %). In addition, Al (11.47 %), Cu (4.47 %), Pb (2.93 %) and As (2.19 %) extracted in F2 step, may pose a threat if the environment becomes

acidic. The highest potential risk comes from Al, due to its high yields in F2 and high pseudo-total content.

Distribution of various metals and metalloids in BR samples varies from one deposit to another, due to different BR chemical, mineral composition and pH.^{10,11} The ecological risks coming from labile Al and Cr forms were recognised considering alkaline BR samples from Ajka (Hungary)¹¹ and Alcoa (Spain).¹⁰ Conversely, lower solubility of Al and only trace amounts of labile Cr(VI) were found in neutralised BR from Kidričevo (Slovenia),¹¹ suggesting that neutralised form is environmentally more acceptable.

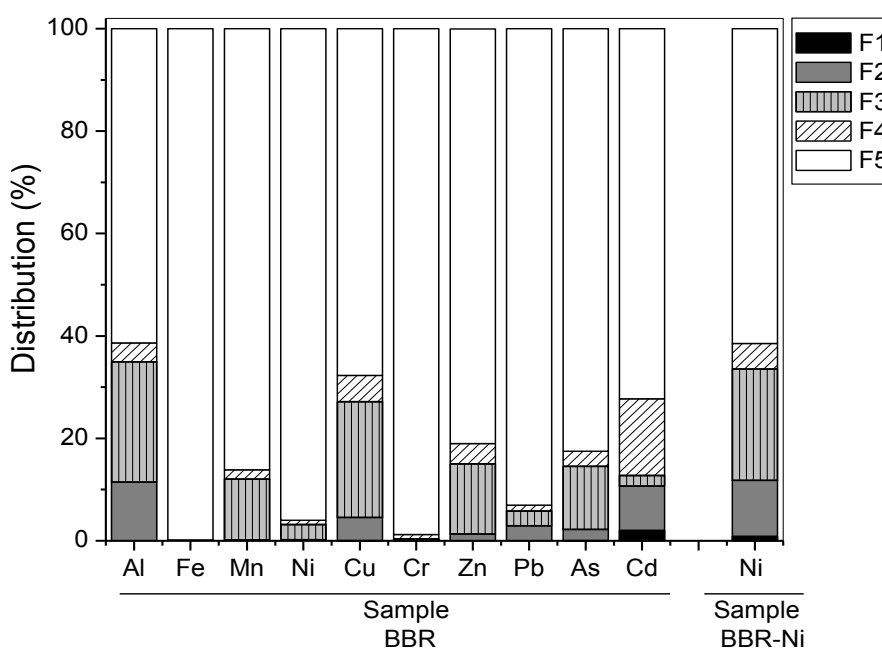


Figure 1: Distribution of selected elements in samples BBR and BBR-Ni

In reaction with BBR, Ni was converted from soluble (ionic) to more stable form. Considering sample BBR-Ni, 61.49 % of pseudo-total Ni was found in F5, 21.67 % in F3 and 10.94 % in F2, whereas only 0.87 % in F1 (Figure 1). Thus, the mobility of Ni was increased in respect to its original distribution, but still fairly low. Considering both high sorption capacity towards Ni,¹⁴ and low mobility, BBR can be considered as a promising immobilisation agent.

Conclusions

Although the pseudo-total amounts of some toxic elements contained in BBR were high, sequential extraction analysis indicated their low mobility given that 61.35 -

99.87 % of their content was located in the residual phase. In the most labile fraction F1, the presence of investigated elements was negligible except for Cr. Potential risks may also arise from metals detected in F2: Cu, Pb and As were found in the amounts of 2.17-4.47 %, but the emphasis is on Al which is a macro-element distributed in F2 with 11.47 %. In BBR-Ni sample, Ni was primarily bound in phases F5 and F3, which signifies strong immobilisation. Results of this study are encouraging for the continuing research of BR as an alternative for natural mineral sorbents in the immobilisation of toxic heavy metals and radionuclides. As higher detected mobility of Al and Cr can be connected with high pH of raw sample, BBR forms neutralised by different methods and to different pH values should also be analysed by sequential extraction, for comparison.

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References

1. M. Komárek, A. Vanek and V. Ettler, "Chemical Stabilisation of Metals and Arsenic in Contaminated Soils Using Oxides, A Review", *Environ. Pollut.*, **172** 9-22 (2013).
2. EPA 542-R-07-013, "The Use of Soil Amendments for Remediation, Revitalisation and Reuse", 2007.
3. IAEA Technical Report Series no. 408, "Application of Ion Exchange Processes for the Treatment of Radioactive Waste and Management of Spent Ion Exchangers", International Atomic Energy Agency, Vienna, 2002.
4. M. Ahmaruzzaman, "Industrial Wastes as Low-cost Potential Adsorbents for the Treatment of Wastewater Laden with Heavy Metals", *Adv. Colloid Interface Sci.*, **166** (1-2) 36-59 (2011).
5. C. Klauber, M. Gräfe and G. Power, "Bauxite Residue Issues: II. Options for Residue Utilisation", *Hydrometallurgy*, **108** (1-2) 11-32 (2011).
6. W. Liu, J. Yang and B. Xiao, "Review On Treatment And Utilisation Of Bauxite Residues In China", *Int. J. Miner. Process.*, **93** (3-4) 220-231 (2009).
7. S. Wang, H. M. Ang and M. O. Tade, "Novel Applications Of Red Mud As Coagulant, Adsorbent And Catalyst For Environmentally Benign Processes", *Chemosphere*, **72** (11) 1621-1635 (2008).
8. G. Power, M. Gräfe and C. Klauber, "Bauxite Residue Issues: I. Current Management, Disposal and Storage Practices", *Hydrometallurgy*, **108** (1-2) 33-45 (2011).
9. L.Y. Li, "Properties of Red Mud Tailings Produced Under Varying Process Conditions", *J. Environ. Eng.*, **124** (3) 254-264 (1998).
10. D. A. Rubinos and M. T. Barral, "Fractionation and Mobility of Metals in Bauxite Red Mud", *Environ. Sci. Pollut. Res.*, **20** (11) 7787-7802 (2013).
11. R. Milačič, T. Zuliani and J. Ščančar, "Environmental Impact of Toxic Elements in Red Mud Studied by Fractionation and Speciation Procedures", *Sci. Total Environ.*, **426** 359-365 (2012).
12. A. Tessier, P. G. C. Campbell and M. Bisson, "Sequential extraction procedure for the speciation of particulate trace metals", *Anal. Chem.*, **51** (7) 844-860 (1979).

13. D. Petrović, M. Todorović, D. Manojlović and V. D. Krsmanović, "Speciations of Trace Metals in the Accumulation Bogovina on the Crni Timok River", *Pol. J. Environ. Stud.*, **18** (5) 873–884 (2009).
14. I. Smičiklas, S. Smiljanić, A. Perić-Grujić, M. Šljivić-Ivanović and D. Antonović, "The Influence of Citrate Anion on Ni(II) Removal by Raw Red Mud from Aluminum Industry", *Chem. Eng. J.*, **214** 327-335 (2013).

