

Red mud and fly ash for remediation of mine sites contaminated with As, Cd, Cu, Pb and Zn

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Abstract

The paper presents the results of a laboratory investigation conducted for assessing the feasibility of immobilising the heavy metals (As, Cd, Cu, Pb and Zn) contained in a disused mine tailings dam. Samples of tailings were mixed with relatively small proportions of bauxite red mud and power station fly ash. The sorption capacity of these two materials, already determined for Cd, Cu, Pb and Zn, has been determined here for arsenic by means of batch experiments on purposely prepared solutions. The results of this preliminary investigation show that sorption capacity is strongly influenced by pH. While the red mud performs better at low pH, the ability of fly ash to adsorb As increases with increasing pH. Tests carried out in leach columns containing tailings alone and tailings mixed with 15% by weight neutralized red mud or fly ash demonstrate the heavy metal sorption potential of the two materials, the red mud proving to be the more effective.

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1. Introduction

In many countries, the gradual cessation of mining activity, accompanied by the lack of post-closure care for safeguarding the areas from contamination, has left behind a devastating legacy in both socio-economic and environmental terms. As a result, measures need to be taken to remediate former mine sites in areas often abounding in natural resources and with a rich industrial heritage.

There are essentially two causes of heavy metal pollution in these areas:

- acid mine drainage rising up through the soil horizons leaching out the heavy metals, transporting and redepositing them often at some distance from the pollution source;
- mine spoil dumps, metallurgical and mineral processing wastes.

Environmental remediation technologies include in situ or ex situ techniques for decontaminating the polluted soils, such as soil-washing, physical separation, biological treatment, phytoremediation, and leaching. In line with EU and national recommendations, the current tendency is to develop and implement in situ techniques where possible so as to minimize disturbance of contaminated terrains.

In the event that definitive solutions for reducing the concentrations to below the legal limits are not economically or technically feasible, then safety measures are required to ensure source isolation and containment. This can be accomplished by means of immobilisation techniques, using suitable additives for minimising the release of contaminants into the environment.

Increasing attention is being focused on the possibility of using industrial processing waste for heavy metal immobilisation, in the strive to reduce the quantity of material to be disposed of, yielding economic and environmental benefits. In this regard, several studies have been conducted using as additives for heavy metal removal the untreated or variously stabilized red mud residues produced by the Bayer process for alumina refining and fly ash generated by coal-fired power stations [1–5].

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The experimental investigation described here intends to further contribute to the development of immobilisation techniques, exploring the possibility of using the red mud produced by the Eurallumina company at Portovesme in SW Sardinia, Italy and fly ash from a coal-fired power station operating in the same area for remediating sites contaminated with arsenic and other heavy metals. The investigation comprised two stages. In the first stage, we performed reactor tests to evaluate the ability of the two waste materials to remove As from purposely prepared solutions, following the same procedure used earlier for the heavy metals Pb, Zn, Cu, Cd, and Mn [6,7]. The second stage consisted in determining the As (and other heavy metals) sorption capacity of red mud and fly ash. Tests were carried out using three plexiglass leach columns, the first containing a sample of contaminated mine tailings, the second the same tailings mixed with red mud and the third tailings mixed with fly ash. The same quantity of leach solution was used throughout.

2. Materials

2.1. Red mud

Chemical composition of the red mud used in the tests was determined by means of a Thermo Jarrell Ash Atom Scan 25 ICP (inductively coupled plasma) spectrometer. LOI (loss of ignition) was determined at 750 °C in accordance with ASTM D5142-02a [8]. Results are shown in Table 1.

Mineralogical determinations using X-ray diffractometry revealed the main constituents of the red mud to be: aluminium in the form of boehmite and gibbsite, haematite, cancrinite, ilmenite, rutile and quartz. The pH, measured by adding deionized water to the tailings at a solid-to-liquid ratio of 1:2.5 following Italian standard soil analysis procedures [9], was 10.67. Specific gravity, determined using an AccuPyc 1330 gas picnometer manufactured by Micromeritics Instruments, was 2.77 g/cm³, while surface area determined using the N₂ BET method was 31.8 m²/g.

Because of their highly caustic nature, red muds are classified as hazardous waste and as such are required to be neutralised prior to transport, even if they are to be reused. For this reason, as suggested by other researchers [1,4], we first treated the red mud with seawater to lower the sodium concentration, thereby reducing the pH to environmentally acceptable levels.

The mud was then filtered and dried and pH measured again following the described above procedure, giving a value of 8.71.

2.2. Fly ash

We used fly ash from the Portovesme power station in SW Sardinia in the experimental tests. Chemical composi-

Table 2
Chemical analyses of Portovesme fly ash

SiO ₂ (%)	37.31	Na ₂ O (%)	7.69	MnO (%)	0.04
Al ₂ O ₃ (%)	22.81	K ₂ O (%)	1.18	Pb (ppm)	75
Fe ₂ O ₃ (%)	3.31	TiO ₂ (%)	1.16	Zn (ppm)	550
CaO (%)	9.44	P ₂ O ₅ (%)	0.73	Cd (ppm)	25
MgO (%)	7.73	LOI (%)	8.49	Cu (ppm)	53

Table 3
Grain size analysis and LOI of fly ash

Size class (µm)	Mass (%)	LOI (%)	LOI distribution (%)
+45	27.99	20.80	68.3
−45+37	7.78	5.91	5.4
−37	64.34	3.46	26.3
Total	100.00	8.49	100.0

tion determined by means of ICP spectrometry is shown in Table 2.

LOI (loss of ignition) was determined at 750 °C in accordance with ASTM D5142-02a [8]. pH and specific gravity, measured using the same procedure as for the red mud, were 12.17 and 2.24 g/cm³, respectively. Surface area determined using the N₂ BET method was 3.6 m²/g.

Microscopy investigation confirmed that the non-combustible fraction is characterised by individual, mainly spherical particles, while the carbon phase consists of irregularly shaped, highly porous particles, often clustered together. Diffractometric analysis revealed the presence of mullite and of a phase similar to graphite that may well correspond to the product of coking. Magnetite is also present as the final step of pyrite oxidation. Microprobe investigation showed the majority of the fly ash to consist of an amorphous phase with extremely variable chemical composition.

Observation on polished briquettes showed the unburnt coal particles to exhibit varying degrees of transformation, limitedly to the thin outer shell in the case of compact elements, which are also characterized by the presence of a dispersed vitreous phase, or deep within the particles in the case of porous matter. Presumably, the former originate from macerals such as inertinite and exinite, the latter from vitrinite [7]. Grain size analysis, shown in Table 3, indicated that the residual combustible fraction tends to concentrate in the coarser size fractions.

2.3. Contaminated waste

Immobilisation tests were performed on a sample of material collected from the tailings pond of the Bacchu Locci flotation plant in SE Sardinia, which operated in the 1950s and 1960s.

Table 1
Chemical analysis of red mud (Eurallumina)

SiO ₂ (%)	9.58	Na ₂ O (%)	12.06	Cu (ppm)	35	V (ppm)	1476
Al ₂ O ₃ (%)	17.91	K ₂ O (%)	0.30	Pb (ppm)	144	Ba (ppm)	206
Fe ₂ O ₃ (%)	30.45	TiO ₂ (%)	8.61	As (ppm)	62	Cd (ppm)	23
CaO (%)	7.77	P ₂ O ₅ (%)	0.20	Zn (ppm)	506	Cr (ppm)	1237
MgO (%)	0.86	LOI (%)	12.38	Zr (ppm)	1150	Hg (ppm)	0.7

Table 4
Chemical analysis of mine tailings

Al ₂ O ₃ (%)	8.85	K ₂ O (%)	2.29	LOI (%)	17.74	Au (ppm)	4.91	Ni (ppm)	25.8
Fe ₂ O ₃ (%)	10.69	TiO ₂ (%)	0.38	C (%)	1.27	Cd (ppm)	1827	Pb (ppm)	101712
CaO (%)	1.64	P ₂ O ₅ (%)	0.12	S (%)	3.76	Cu (ppm)	999.6	U (ppm)	15
Na ₂ O (%)	0.13	MnO (%)	0.05	Ag (ppm)	288.3	Cr (ppm)	120	V (ppm)	103
MgO (%)	0.05	SiO ₂ (%)	41.71	As (ppm)	58952	Hg (ppm)	0.624	Zn (ppm)	1376

The sample was chemically and mineralogically characterised and grain size distribution determined.

Chemical determinations using ICP spectroscopy are shown in Table 4. A pH of 2.83 was determined following the procedure described above.

Mineralogical analysis conducted by means of SEM and X-ray diffractometry indicated quartz, gypsum and muscovite as the main constituents of the country rock. As for metallic minerals, the only sulphide species identified was arsenopyrite, the chief constituent of the ore deposit. All the other metallic minerals occur in the form of oxides, the weathering product of the primary sulphide minerals (pyrite, arsenopyrite, galena and blende, etc.). The oxidised components of particular importance include scorodite (arsenate of iron) and anglesite.

Grain size analysis, shown in Table 5, also revealed the presence of tailings with grain sizes larger than those usually treated in flotation plants.

3. Experimental

The investigation was conducted using mechanically stirred reactors and leaching columns. Experiments using stirred reactors were conducted both for evaluating the As removal ability of red mud and fly ash from purposely prepared solutions as well as for determining heavy metal release into distilled water from the mine tailings or the tailings admixed with red mud or fly ash. We performed leach column tests to investigate the possibility of significantly reducing the concentration of As and other heavy metals in the eluate by admixing the contaminated tailings with suitable amounts of the two waste materials.

3.1. Mechanically stirred reactors

3.1.1. Arsenic removal using red mud

To evaluate the influence of pH on the ability of seawater neutralised red mud to remove As, we used different start-

Table 5
Grain size analysis of mine tailings

Grain size class (mm)	Mass (%)
+10	21.85
–10+5	6.84
–5+2	11.34
–2+1	7.75
–1+0.5	9.28
–0.5+0.1	26.05
–0.1	16.89
Total	100.00

ing solutions varying the pH with HNO₃ or NaOH additions. Tests were performed in mechanically stirred reactors fitted with teflon baffles, setting speed to 70 rpm, on a 10 mg/l arsenic solution with pH of 2.6. The solution was prepared either from Na₂HAsO₄·7H₂O salts (test 1) or from a 1000 mg/l As(v) ICP Standard solution (test 2), supplied by *Exaxol Italia S.r.l.* Upon completion of each 24-h test performed using 2 g of red muds in 190 ml of solution, the solid and liquid fractions were separated by vacuum filtration using a Buchner funnel and 0.45 μm filter. An SS-7 DCP (Direct Current Plasma) spectrometer, manufactured by ARL was used to determine the residual arsenic concentration in the liquid fraction.

Fig. 1 shows for tests 1 and 2 the amount of As removed from solution, expressed in mg of As per gram of red mud, versus pH measured at the end of the test. The results show, in agreement with the literature data [10–12], that the sorption capacity of the neutralised red mud is greater at the lower pH values. Arsenic removal decreases with increasing pH notwithstanding the fact that in the pH range 7–11 this element occurs mainly in the form of HAsO₄²⁻ [13], the reason being that it has to compete with the hydroxide ion. What is more [14–16], at a pH of over 8 the zeta potential of the red mud gradually evolves from positive to negative.

A similar investigation conducted under the same experimental conditions but using untreated red mud, showed sorption capacity to diminish rapidly at pH of over 4 and the amount of As removed to be much lower than for the stabilised material [10,17].

3.1.2. Arsenic removal using fly ash

Similarly to the red mud, the investigation was conducted in mechanically stirred reactors using a 10 mg/l arsenic solution with pH of 2.6 prepared from a 1000 mg/l As(v) ICP Standard solution supplied by *Exaxol Italia S.r.l.* Experiments were car-

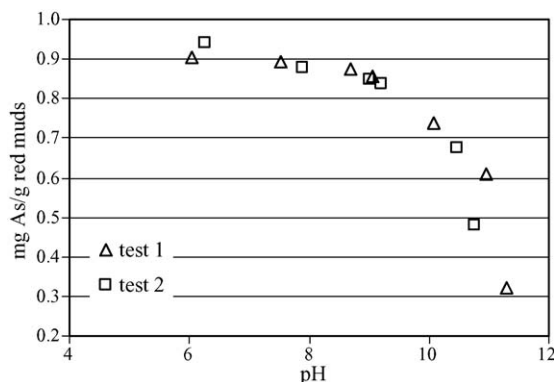


Fig. 1. As removed (mg) per g of red mud, vs. pH.

Table 6
pH of starting solution, solution + fly ash and final solution

	Sample							
	1	2	3	4	5	6	7	8
Starting solution	1.90	2.00	2.20	2.60	2.80	3.00	4.00	4.5
Solution + fly ash	2.25	2.90	3.07	5.80	6.90	8.30	9.40	9.71
Final solution	3.40	6.85	7.40	8.45	9.35	9.74	10.05	10.64

ried out varying the following parameters: solution pH; arsenic concentration in solution; amount of substrate. The influence of each of the above variables is discussed below.

In order to evaluate the influence of pH, five beakers were prepared containing 190 ml of a 10 mg/l As solution varying the pH with HNO₃ or NaOH additions. Two grams of fly ash were then added to each beaker and the mixture was stirred constantly for 24 h. Afterwards pH was determined and As analysed as described above.

Table 6 shows solution pH after adjustment with HNO₃ or NaOH, after fly ash addition and after 24 h. Fig. 2 shows the amount of As removed from solution expressed in mg As per g of fly ash versus ultimate pH.

Unlike the red mud, for the fly ash solution arsenic removal increases with pH, as shown in Fig. 2. This behaviour may be explained by the presence of Ca and other cations, as insoluble arsenates probably form when Ca²⁺ is present [18,19]. Further, we should also point out that in water the amorphous silica contained in the fly ash reacts with hydrated lime to form calcium silicate hydrates (pozzolanic reaction). This reaction produces a sorbent material with greater porosity and larger surface area than the original fly ash [20–22].

Clearly, a more detailed investigation into the surface characteristics of the fly ash used in the tests is necessary to better interpret the correlation determined. Over the pH range tested, maximum removal of 0.73 mg As per g of fly ash was achieved at pH 10.64.

We conducted two experiments for determining the influence of arsenic concentration in solution on the sorption capacity of fly ash: in the first (test A) we used 190 ml of a 9.85 mg/l As starting solution, in the second (test B) 790 ml of a 2.4 mg/l As starting solution adding 2 g of fly ash in both tests. In this way we were able to conduct tests at a practically constant milliequiv-

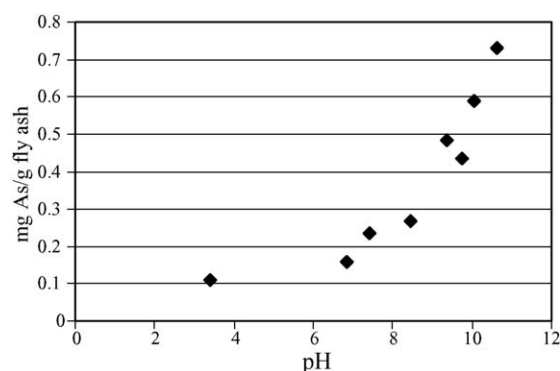


Fig. 2. As removed (mg) per g of fly ash, vs. pH.

Table 7

Arsenic removal from starting solutions with different As concentrations and constant amount of substrate

	Solution	As in solution (mg/l)	pH	As removed (mg/g)	As removed (%)
Test A	Starting	9.85	2.69		
	After 24 h	4.96	9.14	0.46	49.64
Test B	Starting	2.40	2.75		
	After 24 h	1.64	9.38	0.30	31.67

alent ratio of arsenic per gram of fly ash. Tests and analytical determinations were performed as described above.

Table 7 shows arsenic concentration in solution, pH determined at the end of the test, amount of arsenic removed per g of fly ash as well as removal efficiency for each test.

The results show that the amount of As removed per g of fly ash increases with As concentration of starting solutions.

The influence of the amount of substrate was evaluated keeping starting solutions unchanged (190 ml of 9.85 mg/l As solution) and varying fly ash weight (0.5–1–2–3 g). Consequently, the ratio between milliequivalents of arsenic in solution and amount of substrate changes. Table 8 shows the amount of fly ash used in the test, initial As solution concentration and concentration after 24 h, the respective pH determinations and amount of As removed both in terms of mg As per g of fly ash and percent of starting concentration.

The results show that the amount of As removed, expressed both as mg per g of fly ash and percent of starting concentration, increases with the amount of fly ash used. This is due to the fact that as the amount of sorbent increases so too does the pH.

3.2. Metal leaching tests on contaminated tailings, with or without immobilising agents

Metal leaching tests were performed in distilled water using the –5 mm grain size fraction of samples of as received contaminated mine tailings and the same samples admixed with either red mud or fly ash as immobilising agents.

Experimental conditions were as follows:

- Test A: 50 g tailings + 500 ml distilled water;
- Test B: 50 g tailings + 20 g red muds + 500 ml distilled water;
- Test C: 50 g tailings + 20 g fly ash + 500 ml distilled water.

Table 8

Arsenic removed vs. amount of fly ash used

	Fly ash (g)	As in solution (mg/l)	pH	As removed (mg/g)	As removed (%)
Starting solution		9.85	2.69		
Test C	0.5	9.32	6.85	0.2	5.36
Test D	1	8.12	8.45	0.33	17.58
Test E	2	4.96	9.14	0.46	49.69
Test F	3	1.38	9.35	0.54	85.98

Table 9
Results of metal leaching tests in distilled water

	pH	Zn (mg/l)	Cu (mg/l)	Pb (mg/l)	Cd (mg/l)	As (mg/l)
Test A	2.70	8.112	1.330	4.755	0.072	2.376
Test B	7.16	0.034	<0.002	0.434	<0.005	0.401
Test C	7.18	<0.006	<0.002	<0.02	0.019	0.300

After 24 h the solid and liquid fractions were separated by vacuum filtration using a Buchner funnel and a 0.45 µm filter. Metal concentration in the eluate was determined analysing the liquid fraction using an SS-7 DCP (direct current plasma) spectrometer, manufactured by ARL. Table 9 shows the results of the analyses (the symbol < denotes that the values observed are below the instrument's detectability limit) and the pH values determined at the end of the test.

3.3. Leaching column experiments

Based on the metal leaching test results, an experimental investigation was conducted to assess the feasibility of immobilising the heavy metals contained in the contaminated mine tailings examined, by admixing with red mud or fly ash.

Experiments were performed in three 30 cm high, 41 mm diameter plexiglass columns. The material was kept at the bottom of the column by means of a filter system, consisting bottom upwards of a perforated plexiglass disc overlain by a rock wool disc in turn overlain by a 2 cm thick layer of glass balls.

Column 1 was filled with 300 g of as received contaminated mine tailings, column 2 with 300 g of as received tailings mixed with 15% by weight red mud (45 g), column 3 with 300 g of as received tailings mixed with 15% by weight fly ash.

Experimental conditions were as follows:

- the solid material was agglomerated with 10% by weight distilled water and mixed in rotating cylindrical drums;
- the leaching column was filled with the agglomerated material which was then compacted and aged for 72 h before commencing the tests;
- 150 ml of leach solution (distilled water) was introduced into the column using the pulse method in a single addition every day;
- flowrate, pH (Hanna Instruments HI 92240 pH-meter), conductivity (LF 92 WTW conductimeter) as well as As, Pb, Zn, Cd and Cu concentrations (SS-7 DCP ARL spectrometer) of the effluent were determined daily at the beginning of the test, then every 2–3 days, passing to every week.

The experiment lasted for 80 days. Figs. 3–8 show the pH values (measured daily) and cumulative concentration, expressed in mg of As, Pb, Zn, Cd and Cu in the percolating solution for the three columns versus eluate volume. During the tests we noticed that solution flow rate was higher in column 3, presumably because of the pozzolanic properties of fly ash. The same behaviour has been observed in earlier experiments [2].

As can be observed from the results:

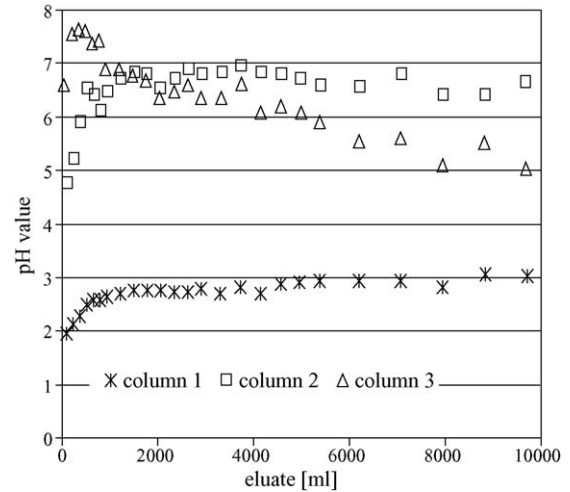


Fig. 3. pH vs. amount of solution percolating through the columns.

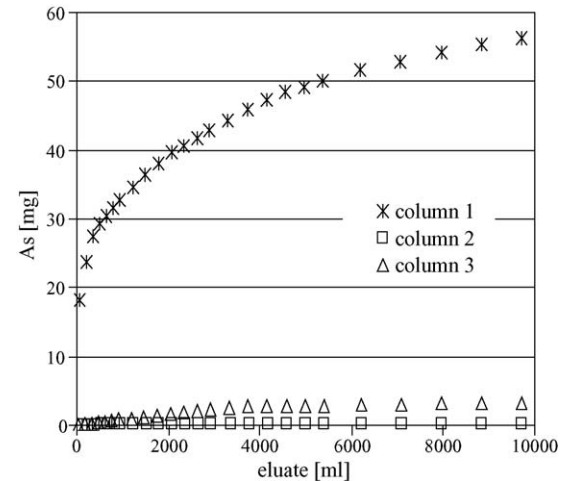


Fig. 4. Cumulative amount of As vs. eluate volume.

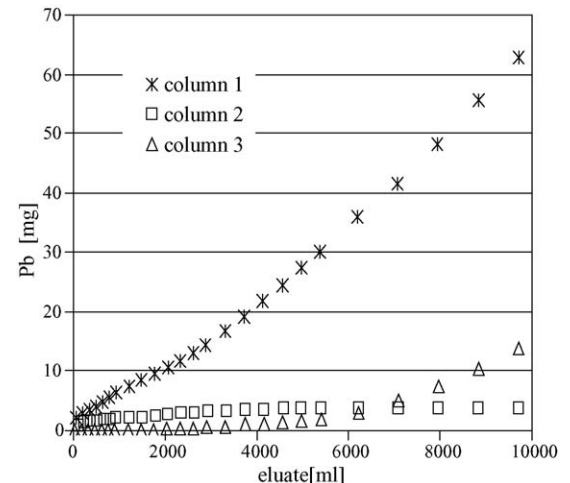


Fig. 5. Cumulative amount of Pb vs. eluate volume.

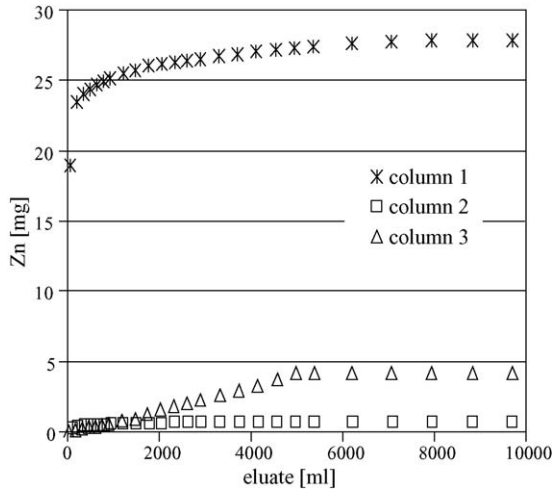


Fig. 6. Cumulative amount of Zn vs. eluate volume.

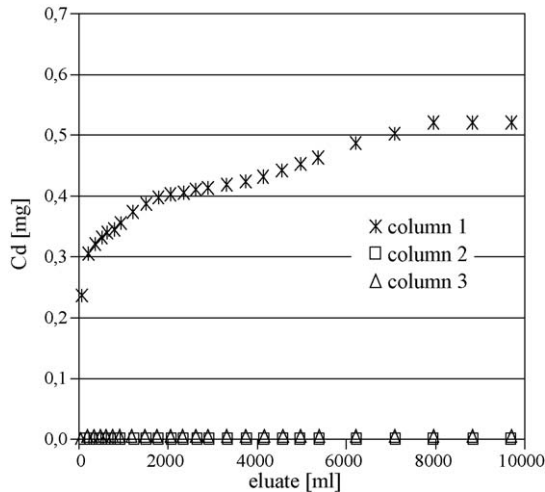


Fig. 7. Cumulative amount of Cd vs. eluate volume.

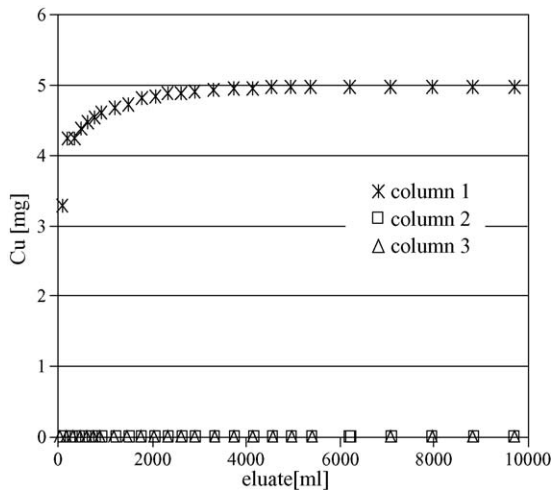


Fig. 8. Cumulative amount of Cu vs. eluate volume.

- pH values for column 1 range between 1.94 and 3.03, increasing over time. pH in column 2 ranges from 4.8 to 6.9 increasing in the first 5 days and remaining practically steady thereafter, while in column 3 values range from 7.6 to 5.0, decreasing over time;
- conductivity in all three columns decreases as volume of percolating solution increases, ranging from 11.13 to 0.6 mS/cm in column 1, 12.69 to 0.59 mS/cm in column 2 and 6.63 to 0.15 mS/cm in column 3;
- arsenic concentration measured in column 1 on the first 3 days is 252.80 mg/l (72.1 ml percolating solution), 39.37 mg/l (213.2 ml percolating solution) and 25.83 mg/l (355.9 ml percolating solution), respectively. Though these concentrations decrease as percolating solution volume increases, they always exceed the limit of 0.5 mg/l established by current Italian legislation for discharge into surface waters [23]. The total amount of As released into 9706 ml distilled water over 80 days is 56.20 mg, half of which was leached out in the first 4 days. The As concentrations in columns 2 and 3 decrease for increasing percolating solution volumes down to values below the instrument's detectability limit (0.08 mg/l). In particular, in column 2 As concentrations were always found to fall within the established limit and the total amount of As released was 0.26 mg. Initially the concentrations observed in column 3 vary between 1 and 0.6 mg/l and only after percolating 2903 ml through the column does the concentration fall below the established limit of 0.5 mg/l. In this case, a total of 3.21 mg of As was leached out;
- Pb concentration in column 1, fluctuates between 3.7 and 8.5 mg/l, a total of 62.7 mg Pb being released. The Pb concentration in column 2 was found to decrease upon reaching an initial peak of 3.87 mg/l, dropping to values below the legal limit (0.2 mg/l) for a volume of percolating solution of around 4500 ml. The opposite trend is observed in column 3 where for a percolating solution volume of 2500 ml the Pb concentration remains below 0.2 mg/l, only to increase gradually up to around 4 mg/l. This behaviour may be associated with the drop in pH observed during the test. The total amount of Pb released by columns 2 and 3 was 3.65 and 13.8 mg, respectively;
- Zn concentrations of 263.40 mg/l (percolating solution volume 72.1 ml) on day 1 and 31.7 mg/l (percolating solution volume 213.2 ml) on day 2 are observed in column 1. The concentrations then gradually diminish from 4 mg/l down to values below the regulatory limit (0.5 mg/l) for a percolating volume of around 2200 ml. The Zn concentration in column 2 is always observed to remain below the 0.5 mg/l limit, while in column 3 it fluctuates between 1.7 and 0.4 mg/l. The zinc leached out of the three columns amounts to 27.88 mg in column 1, 0.70 mg in column 2 and 10.97 mg in column 3;
- Cd concentration in column 1 decreases over time from 3.3 mg/l down to values below the established limits by Italian law (0.02 mg/l) after percolation of a volume of around 2000 ml. Total Cd released amounts to 0.52 mg. The concentration of Cd in columns 2 and 3 was always found to be below the instrument's detectability limit (0.005 mg/l);

- Cu concentrations in column 1, are 45.6 mg/l on day 1 (percolating solution volume of 72.1 ml) and 6.8 mg/l on day 2 (volume 213.2 ml), after which the Cu concentration decreases gradually from 1.44 mg/l to values below the regulatory limit (0.1 mg/l) for a percolating solution volume of around 2500 ml. A total of 5.2 mg copper was leached out from solution. The concentration of Cd in columns 2 and 3 was always found to be below the instrument's detectability limit (0.002 mg/l).

4. Discussion

Based on the experimental findings, the following considerations can be drawn:

- the efficiency of red mud as an immobilizing agent for arsenic and other heavy metals has been demonstrated also for extremely complex situations, as in the case study described here concerning highly aggressive mine waste. In fact, the As, Zn, Cd and Cu concentrations in the eluate fall in all cases below the limits established by Italian regulations for discharge into surface waters [23]. The Pb concentration in the eluate is always well below the initial value observed in the column containing tailings alone, but only falls below the acceptable limit after 4500 ml of solution have passed through the column. At the end of the test, the amount of As, Pb and Zn released in column 2 is 216, 17 and 40 times lower than column 1, while concentrations in Cd and Cu are below the instrument's detectability limits;
- the use of fly ash to immobilize arsenic and other heavy metals makes it possible to reduce their concentrations in the eluates. In particular, the Cd and Cu concentrations are always observed to be below the acceptable limit. On the other hand, though the As content in the eluate is always lower than the as-received tailings, concentrations only fall below the Italian regulatory limit after 2900 ml of solution have passed through the column. As already mentioned, the Zn concentration fluctuates between 1.7 and 0.4 mg/l, irrespective of the amount of solution percolating through the column. As for Pb, we observed concentrations below the established limits in the early experimental stages, the values tending to gradually increase though always remaining lower than column 1. At the end of the test, the total amount of As, Pb and Zn released by column 3 is roughly 17.5, 4.5 and 2.5 times lower than the concentrations observed in column 1; while the Cd and Cu concentrations are below the instrument's detectability limits.

Thus, the experimental investigation conducted here demonstrates that both red mud and fly ash are able to significantly reduce the concentrations of As and the other heavy metals examined in eluates from mine tailings. However, the red mud performs comparatively better, inasmuch as this material appears better able to adapt to the highly acidic pH conditions of the contaminated waste examined here (pH 2.83). Leach column tests showed that the red mud stabilises the pH of the percolating solution at values of around 6–6.5, while maintaining a

sufficiently high sorption capacity. By contrast, after reaching an initial value of 7.6 the pH of the solution percolating through the column containing fly ash tends to decrease over time down to values of around 5. Their sorption capacity diminishes at these values, releasing contaminants into solution.

For a better understanding of the results obtained, which requires a more in-depth investigation, we also need to take into account their different surface characteristics, surface area – which is about ten times higher in red mud than in fly ash – and chemical and mineralogical composition. The red mud exhibits greater sorption capacity than the fly ash, probably because it contains larger amounts of Fe and Al oxides and hydroxides (which are generally used in water treatment processes for removing metals by means of co-precipitation and adsorption mechanisms [24–26]), has larger surface area and stabilises the pH at acceptable values.

5. Conclusions

We have explored the potential use of red mud produced at the Portovesme bauxite refinery in SW Sardinia and fly ash generated at a coal-fired power station located in the same area, for remediating contaminated mine sites. Tests were carried out on samples of highly acidic material containing high proportions of As, Cd, Cu, Pb and Zn taken from the tailings pond of the Baccu Locci flotation plant in SE Sardinia. The experimental investigation conducted in mechanically stirred reactors – a follow up to earlier studies conducted on Pb, Zn, Cd and Cu removal – using purposely prepared solutions, demonstrated the As removal potential of the red mud and fly ash tested. The results indicate that the sorption capacity of the two waste materials is strongly influenced by solution pH. The red mud performs better at low pH values while the ability of fly ash to remove As increases with increasing pH.

Column tests have shown that both waste materials significantly reduce As, Cd, Cu, Pb and Zn release into the eluate. Further, the red mud was found to remove As, Pb and Zn more efficiently probably because it is better able to adapt to the highly acidic mine tailings used in the experiments.

Though further investigations are necessary to provide a comprehensive interpretation of the results obtained, the larger amount of Fe and Al oxides and hydroxides contained in the red mud, as well as its larger surface area and stability at just below neutral pH, may explain why it is a more effective metal immobilizing agent than fly ash.

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