

Article

Synergism Red Mud-Acid Mine Drainage as a Sustainable Solution for Neutralizing and Immobilizing Hazardous Elements

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Abstract: Acid mine drainage (AMD) and red mud (RM) are frequently available in the metallurgical and mining industry. Treating AMD solutions require the generation of enough alkalinity to neutralize the acidity excess. RM, recognized as a waste generating high alkalinity solution when it is in contact with water, was chosen to treat AMD from South Africa at room temperature. A German and a Greek RM have been evaluated as a potential low-cost material to neutralize and immobilize harmful chemical ions from AMD. Results showed that heavy metals and other hazardous elements such as As, Se, Cd, and Zn had been immobilized in the mineral phase. According to European environmental standards, S and Cr, mainly present in RM, were the only two elements not immobilized below the concentration established for inert waste.

Keywords: acid mine drainage; red mud; neutralization; immobilization; precipitation



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1. Introduction

Acid Mine Drainage (AMD) is a term for wastewaters from mining processes. AMD is a sulfate-based solution concentrating several metallic ions from ores [1,2]. During mining operations, rocks containing sulfide minerals are fragmented, increasing the surface area exposed to water and air, favoring the generation of AMD at high rates [3]. Tabela et al. [4] mentioned that contaminated debris contains several hazardous elements such as arsenic (As), selenium (Se), and boron (B), and heavy metals like cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn). Pollution generated by these naturally contaminated rocks could pose severe problems to living organisms, including surrounding populations living close to mine and disposal sites.

Park et al. [5] mentioned different remediation strategies like neutralization, adsorption, ion exchange, membrane technology, biological mediation, and electrochemical for reducing AMD negative environmental impacts on human health and ecosystems. Nonetheless, complex techniques require high labor, energy, and maintenance costs besides a continuous supply of chemicals and long-term monitoring of AMD on ecosystems and underground waters.

Igarashi et al. [6] treated AMD using a lab-scale continuous ferrite process flow setup removing Cu and As in the first sludge, which is stable in standard leaching tests. Magnetic magnesium-ferrites and magnetite were generated when dissolved Si was low. Nevertheless, the treatment could not neutralize all toxic metallic ions.

AMD from South Africa originates from sulfide conglomerates stored on deposits where the rain rinses the acid and metals such as uranium out of the dumps [3]. Additionally, South Africa has severe limitations on freshwater, with an average rainfall of under 450 mm per year [7]. AMD from South African mines containing around 3500 mg/l [3] of sulfates with pH values between 2 and 3 favor the dissolution of several metals that

can infiltrate groundwater deposits and rivers pathways in areas close to the deposits. Iron sulfides resulting from pyrite (FeS_2) oxidation in contact with air enter in the solution under Fe^{3+} and naturally precipitate in river pathways creating a bright orange trail [8].

AMD waters can be classified by the content of acid and dissolved metals with the Ficklin diagram [9]. At the surface, rain or surface water dilute AMD increase pH values driving to predominantly precipitate aluminates favoring the adsorption of other metallic ions [10]. On the other hand, heavy metals are generally removed by Fe precipitation. Al precipitation only becomes significant when the iron content is low, but this is rarely the case.

Mwewa et al. [11] have studied the synthesis of poly-alumino-ferric sulfate coagulant from acid mine drainage by precipitation reaching the recovery of Fe and Al at pH 5.0, about 99.9 and 94.7% for Fe and Al, respectively. An increase of pH-value up to 7 leads to the overall Al recovery of 99.1%. Although Al precipitation was 99.1% at pH 7, the precipitate formed at pH 5 was chosen for coagulant production due to the reduced risks to co-precipitate other impurities in substantially higher concentrations. Dissolution of precipitate in 5.0% (w/w) sulfuric acid produced a coagulant containing 89.5% Fe and 10.0% Al, which is comparable to the PFS commercial coagulant. This process can be easily integrated into existing AMD treatment plants, providing revenue and minimizing treatment costs, as well as reducing the sludge volume by 95.0%.

Keller et al. [12] have studied the effectiveness of fly ash and RM as strategies for sustainable AMD management. Because of the high alkalinity, German RM is the most promising precipitation agent achieving the highest pH-values. Coal fly ash is less efficient than RM for neutralization and precipitation. Temperature increases adsorption kinetics. In this study, the authors found a maximum pH-value of 6.0 was reached by adding 100 g German RM at 20 °C to AMD-water with an initial pH value of 1.9. RM removed 99% of Al present as hydroxide for a pH 5.0. Some rare-earth elements as Y and Ce precipitate in contact with Greek RM with an efficiency of 50 and 80%, respectively, at 60 °C in 5 min.

Our main aim is to perform a neutralization of AMD using RM from Greece and Germany and to discuss the possibility of recovering valuable metals such as Al, Zn, Mn, and rare earth elements (REE). Using RM leads to the preparation of wastewater for returning into processing or releasing to the environment. Another aim of neutralization with alkaline material is to formulate solid waste materials for further metal winning processes in order to immobilize the hazardous metals.

2. Materials, Characterization and Experimental Procedure

2.1. Materials

The constituent concentration ($\mu\text{g}/\text{L}$) from the eluate obtained from these two bauxite residues: Red Mud from Greece (RM.Gr) and Red mud from Germany (RM.De) will be compared with the concentration of anions and cations in AMD, as shown in Table 1.

The pH of the AMD wastewater ranges around 2.0 in contrast to both red mud with ones above 10. Table 2 compares pollutants' concentration in mg/kg (see Equation (1)) and EU standardized limits to define hazardous, non-hazardous, and inert waste.

For assessing the synergistic effect of AMD combined with RM, materials were mixed using different ratios, keeping the lines of the compliance test EN 124557 but using AMD instead of distilled water.

Kaußen and Friedrich [13] described the mineralogy of the RM.De. No sufficient reference data (known crystallographic measurements) exist to characterize the missing 1.5% accounts unknown or amorphous from bauxite residue mineralogical composition. In the current X-ray diffraction (XRD) full profile fitting mineral phase quantification, it was not possible to quantify amorphous content. Amorphous content can be determined in phase quantification when a known quantity of an internal standard such as corundum is added to the sample. Result showed in Table 3.

Table 1. Concentration of pollutants in µg/L of AMD, RM.Gr (Red Mud from Greece) and RM.De (Red mud from Germany) (RM eluates obtained from the elution test based on EN 12457-2).

Element	AMD	RM.Gr	RM.De
F [mg/L]	8.5	7.5	2.6
Cl [mg/L]	2.8	4.8	0.8
NO ₃ [mg/L]	<0.1	0.3	0.3
SO ₄ [g/L]	16.6	0.1	<0.1
As [µg/L]	15.4	389.5	6.7
Ba [µg/L]	1.9	<0.1	<0.1
Cd [µg/L]	67.8	0.1	<0.1
Cr [µg/L]	34.6	18.4	555.2
Cu [µg/L]	216.2	<5	<5
Mo [µg/L]	<0.1	19.1	<0.1
Ni [µg/L]	982.2	0.2	<0.1
Pb [µg/L]	8.4	<0.1	<0.1
Sb [µg/L]	<0.1	<0.1	<0.1
Se [µg/L]	1.3	11.8	4.0
V [µg/L]	0.6	2,623.4	202.9
Zn [µg/L]	7,250.3	<0.1	<0.1
pH	2.0	10.3	11.3

Table 2. Leaching pollutants from RM in contact with distillate water in mg/kg based on EN 12457-2 compared with the EU standardized limits.

Element [mg/kg]	Limits for Inert Waste	Limits for Non-hazardous Waste	Limits for Hazardous Waste	RM Greece	RM Germany
Cl	800	15,000	25,000	48.07	7.70
F	10	150	500	74.57	25.83
SO ₄	1000	20,000	50,000	1100	37.27
Ni	0.4	10	40	<0.01	<0.01
Pb	0.5	10	50	<0.01	<0.01
Sb	0.06	0.7	5	<0.01	<0.01
Se	0.1	0.5	7	0.12	0.04
Zn	4	50	200	<0.10	<0.10
As	0.5	2	25	3.89	0.07
Ba	20	100	300	<0.01	<0.01
Cd	0.04	1	5	<0.01	<0.01
Cr total	0.5	10	70	0.18	5.55
Cu	2	50	100	<0.05	<0.05
Hg	0.01	0.2	2	<0.01	<0.01
Mo	0.5	10	30	0.19	<0.01

In addition to phases indicated by XRD, Alkan et al. [14] performed a Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN) analysis of Greek red mud. They revealed the presence of large amounts of Fe-, Ca-, Al-, and Si-mixed oxide in red mud, where a certain amount of TiO₂ is entrapped. Due to the heterogeneous nature of this complex oxide, chemical composition and stoichiometry vary through the volume. Therefore, a crystalline phase could not be fully assigned. Varying compositions imply that this complex oxide may be an aggregate or intergrowth of several oxides inherent from Bayer Process.

Table 3. RM mineralogy and quantification [12,13].

Mineral [wt%]	RM.Gr	RM.De
Cancrinite [$\text{Na}_6\text{Ca}_{1.5}\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_{1.6}$]	15	–
Perovskite [CaTiO_3]	4.5	–
Hematite [Fe_2O_3]	30	44
Boehmite [$\text{AlO}(\text{OH})$]	3	13
Goethite [$\text{FeO}(\text{OH})$]	9	–
Anatase [TiO_2]	0.5	5
Calcium aluminium iron silicate hydroxide [$\text{Ca}_3\text{AlFe}(\text{SiO}_4)(\text{OH})_8$]	17	–
Quartz [SiO_2]	2	–
Rutile [TiO_2]	0.5	3
Calcite [CaCO_3]	4	–
Chamosite [$(\text{Fe}^{2+}, \text{Mg})_5\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$]	4	–
Diaspore [$\text{AlO}(\text{OH})$]	9	–
Gibbsite [$\text{Al}(\text{OH})_3$]	2	15
Sodalite [$\text{Na}_4(\text{SiAl})_3\text{O}_{12}\text{Cl}$]	–	7
Nepheline [$\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$]	–	7
Albite [$\text{NaAlSi}_3\text{O}_3$]	–	4
Katoite [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1.5}(\text{OH})_6$]	–	2
%OH-species	12.3	14.0

2.2. Characterization of the Studied Materials

The AMD sample was collected from Mpumalanga, South Africa. All sampling and laboratory analysis was performed in accordance with recognized global standards such as the International Standards Organization (ISO). After sampling and laboratory analysis in South Africa, all samples were sent to Germany. The AMD water was characterized using ICP-OES analysis (SPECTRO ARCOS, SPECTRO Analytical Instruments GmbH, Kleve, Germany) and solid samples by X-ray fluorescence (Axios FAST, Malvern Panalytical GmbH, Kassel, Germany). The AMD was first filtrated in order to remove the formed precipitate, but AMD was not acidified. The solid samples were ground up before the X-ray diffraction analysis (XRD) analysis. Bauxite residue, employed during AMD-treatment as the main raw material, was provided by Aluminum of Greece plant, Metallurgy Business Unit, Mytilineos S.A. (AoG). The sample was first homogenized by using laboratory sampling procedures (riffing method), and then a representative sample was dried in a static furnace at 105 °C for 24 h. Subsequently, the material was milled using a vibratory disc mill, and the sample was fully characterized.

Chemical analyses of major and minor elements were executed via the fusion method (1000 °C for 1 h with a mixture of $\text{Li}_2\text{B}_4\text{O}_7/\text{KNO}_3$ followed by direct dissolution in 10% HNO_3 solution) through a Perkin Elmer 2100 Atomic Absorption Spectrometer (AAS) (Perkin Elmer Inc., Waltham, MA, USA), a Spector Xepos Energy Dispersive X-ray Fluorescence Spectroscopy (ED-XRF, SPECTRO, Kleve, Germany), a Thermo Fisher Scientific X-series 2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Perkin Elmer, Inc., Waltham, MA, USA), and a Perkin Elmer Optima 8000 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Perkin Elmer, Inc., Waltham, MA, USA). In contrast, the loss of ignition (LOI) of the sample was provided by differential thermal analysis (DTA), using a SETARAM TG Labys-DS-C (SETARAM Instrumentation, Caluire, France) system in the temperature range of 25–1000 °C with a 10 °C/min-heating rate, in air atmosphere.

Mineralogical phases were detected by XRD using a Bruker D8 Focus powder diffractometer with nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) coupled with XDB Powder Diffraction Phase Analytical System version 3.107, which evaluated the quantification of mineral phases via profile fitting specifically for bauxite ore and bauxite residues.

2.3. Methodology

As previously mentioned, two types of RM were tested in this study, one from aluminum plants in Greece and another from Germany. For the compliance test EN 124557-2, 90 g of dried RM was mixed with 900 ml of distilled water (L/S 10:1) using PTFE (polytetrafluorethylene) bottles. An end-over-end tumbler was utilized to agitate the samples for 24 h at 6–8 rpm. Leachate volumes are calculated according to Equation (1):

$$L = \left(10 \left[\frac{\text{H}_2\text{O}}{\text{kg}} \right] - \frac{M_c}{100} \left[\frac{\text{H}_2\text{O}}{\text{kg} \cdot \%} \right] \right) \times M_D \quad (1)$$

where:

- L is the volume of used leaching agent (in L);
- M_D is the dry mass of the test portion (in kg);
- M_c is the moisture content ratio (in %).

After 24 h, samples were filtered with a vacuum filtration device, and eluates obtained were post filtered using 0.45 μm membrane filters. Solutions obtained from the elution tests based on the standard EN 12457-2 were analyzed using a Metrohm ion chromatography IC 881 Compact IC Pro (METROHM, Riverview, FL, USA) and an inductively coupled plasma mass spectrometer Agilent 8800 ICP-MS Triple Quad and atomic fluorescence spectrometer for Hg (Analytic Jena GmbH, Jena, Germany). These chemical results in $\mu\text{g/L}$ were used as a reference to compare the anions and cations in solution with AMD.

In order to check the compliance of RM with EU standardized limits, constituent leached from bauxite residues as a function of the original input material is calculated from the following Equation (2):

$$A = C \times \left[\frac{L}{M_D} + \frac{M_c}{100} \right] \quad (2)$$

where:

- A is the release of a constituent at L/S = 10 (in mg/kg of dry matter);
- C is the concentration of a particular constituent in the eluate (in mg/L);
- L is the volume of leachate used (in L);
- M_D is the dry mass of the test portion (in kg);
- M_c is the moisture content ratio (in %).

Mixing AMD/RM was carried out and analyzed using ratios of 90:10, 80:20, 70:30, and 60:40. Each experiment was repeated four times under the same conditions (24 h, 22 °C). Eluates obtained after filtering were compared with the concentration of anions and cations in AMD and eluates from RM under the standard EN 124557-2. Results were presented using the following notation:

- RM10%: RM 10 wt% + AMD 90 wt%
- RM20%: RM 20 wt% + AMD 80 wt%
- RM30%: RM 30 wt% + AMD 70 wt%
- RM40%: RM 40 wt% + AMD 60 wt%
- AMD: 100% solution of acid mining rain
- RM 1:10 H₂O: EN 124557-2 standard elution test with distillate water with liquid/solid ratio 1:10.

After filtering, filter cakes were dried at 80 °C for 72 h and then comminuted below 90 μm employing a planetary ball mill (Fritsch PULVERISETTE 6) for chemical characterization. Chemical composition was analyzed using a PAN analytical WDXRF spectrometer (Malvern Panalytical GmbH, Kassel, Germany) with different internal programs. "Omnia" was used for the quantitative analysis of bulk compounds and "Pro-trace" was used for trace element analysis (lower ppm range). Solutions were also analyzed using IC and ICP-MS technics (Perkin Elmer, Inc., Waltham, MA, USA).

3. Results and Discussion

3.1. pH Influence

According to the elution test EN 12457-2 carried out on these two bauxite residues, these materials cannot be considered inert waste according to the EU landfill directive 1999/31/EC. Besides the leaching outside limits of As, Cr, F, and SO_4 , RM is highly alkaline (see RM1:10H₂O in Figure 1) and needs to be disposed of in special reservoirs.

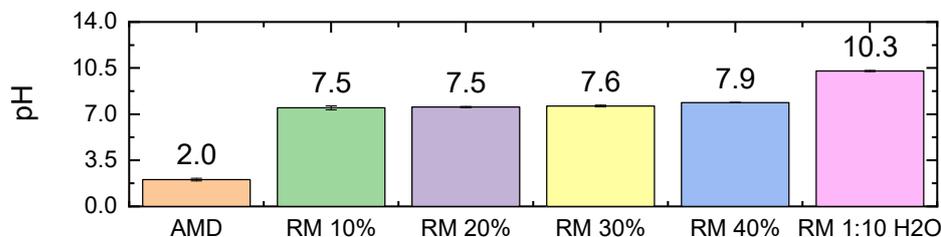


Figure 1. Influence of an addition of Greek RM at pH-value of acid mine drainage (AMD) in 24 h at room temperature.

From the mineralogical quantification carried out by Kaußen and Friedrich [13] on RM.De and Keller et al. [12] on RM.Gr, it can be highlighted that German RM contains 1.7% more hydroxide species than the Greek (see Table 1), explaining its higher pH-value, as shown at Figure 2.

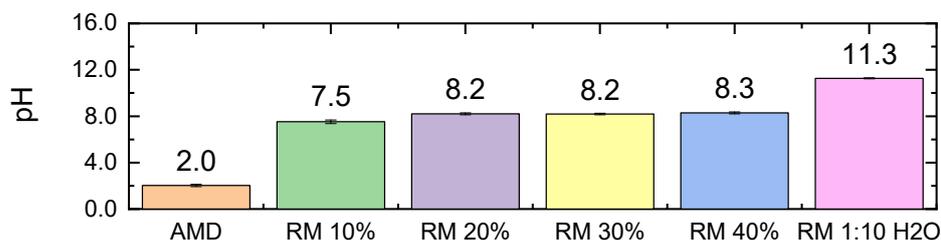


Figure 2. Influence of an addition of German RM at pH-Value of AMD in 24 h at room temperature.

A higher concentration of hydroxides increases RM's ability to react with H^+ cations allowing for improved precipitation of metal ions, many of which are considered hazardous to living organisms.

Previous experiments of Paradis et al. [15] showed that RM has a good neutralization capacity for a short time, but the long-term neutralization potential is uncertain. Thus, brine was added to RM to verify if it can improve long-term alkalinity retention of RM. Therefore, our experiments take time in 24 h but under continuous agitation, which for standard elution test such as EN 12457-2 is one of the worst-case scenarios for natural leaching. Neutralization of both RM and AMD is evidenced by a final pH above 8 and Fe and S precipitation in the mineral phase (see Table 4). The increase of RM over AMD is only preceded by a slight increase of final alkalinity but maintaining pH values between 7.5 and 8.

Table 4. Chemical analysis of compounds after elation tests.

wt%	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	TiO ₂	Fe	S
RM.Gr	6.3	16.3	8.1	2.8	5.2	32.5	0.04
RM.Gr.10	6.2	13.9	10.6	2.6	5.0	34.1	3.39
RM.Gr.20	7.4	16.3	10.2	2.2	5.7	34.6	2.12
RM.Gr.30	7.6	16.8	10.0	2.7	5.6	35.5	1.34
RM.Gr.40	7.9	16.7	10.0	2.9	5.0	34.3	0.95
RM.De	12.3	16.1	6.4	9.1	10.8	20.7	0.02
RM.De.10	13.0	17.0	6.2	8.0	9.9	25.9	1.53
RM.De.20	15.3	19.4	6.4	7.7	10.4	21.5	0.70
RM.De.30	12.7	14.8	6.7	7.5	11.5	28.5	0.50
RM.De.40	11.7	12.7	6.9	7.0	12.3	31.4	0.42

Notation: RM.Gr.XX: mineral obtained after mixing XX wt% RM.Gr and (100-XX) wt% AMD.

3.2. Influence of RM-Addition on Anions Concentration

Figure 3 depicts different anion concentration from both Greek RM (figures on the left side) and German RM (figures on the right side). Addition of 10 wt% RM.Gr decreases the concentration of sulfate ions from 16.8 to 5.4 g/L, as shown in Figure 3a. RM.De shows the same behavior as the Greek, but with concentration falling around 10 g/L, so it was less effective to precipitate sulfate ions (Figure 3e). The leachate limit in terms of sulfate anions becoming hazardous is 5.0 g/L (equivalent to 50,000 mg/kg according to Equation (2)) according to the EU landfill directive 1999/31/EC. An increase in the RM ratio from 10 to 40 % does not lead to a change of anion concentration.

Fluoride anions are present in both AMD and RMs (Figure 3d,h). Results showed a net positive synergistic effect on the AMD-RM mix, preventing these ions from being in the solution.

In contrast to sulfate and fluoride ions, chlorides anions increase in both RMs when the RM ratio increase from 0.1 to 0.4 (see Cl in Figure 3c,g. RM.Gr released two or three times more Cl anions than RM.De. According to XRD results, there is 0.07% Cl in the Greek RM against 0.2% in German RM. Even though there is less Cl available in the Greek RM than in the German, it releases more Cl anions suggesting that it might relate to its mineralogy. Cl in the German RM is concentrated on Sodalite (see Table 3), which is not in the Greek case.

Nitrate anions showed particular behaviors. For one side, its concentration increases with both RMs in contact with AMD compared to the content in AMD and its release from RM in contact with pure water. Perhaps the increase of these anions is related to air penetration in the eluates by the constant mechanical agitation and the reaction between the different compound present in RM with AMD. Gas dissolution in liquids is inversely proportional to an increase in temperature and ions in dissolution. Precipitating most of the ions when the pH is close to neutral values may explain the increase of NO₃ anions in both RMs. It was surprising that both RMs follow different trends, with an NO₃ concentration increase in RM.Gr raising the RM ratio from 0.1 to 0.4. The NO₃ concentration decreased using RM.De instead by using the same RM ratios. Maybe this compartment can be explained by the interaction of different microbial communities that present AMD with the different minerals present in both RMs [16–19].

Nevertheless, after combining different RM and AMD ratios, the concentration of fluoride, nitrate, and chloride ions in the obtained eluates was below the concentration limits for inert waste, 1 and 80 mg/L, respectively, according to Landfill Directive 1999/31/EC.

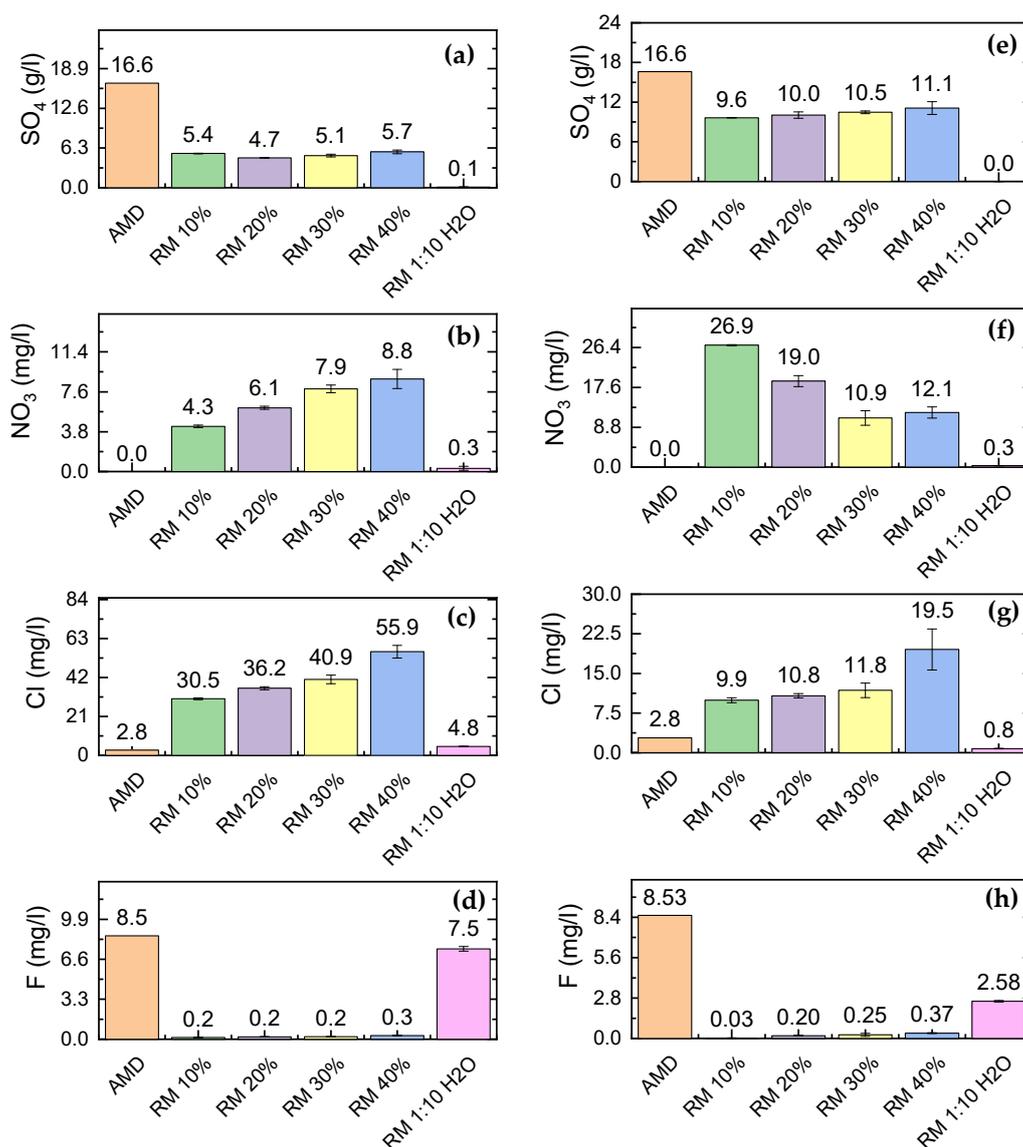


Figure 3. Anion concentration in AMD. RM.Gr (left) and RM.De (right), (a,e) SO₄, (b,f) NO₃, (c,g) Cl, and (d,h) F.

3.3. Influence of RM-Addition on Cation Concentration

Several metallic cations are considered hazardous due to their negative impacts on living organisms and ecosystems. Most of the national and international legislation undergo the content and leaching of these elements: As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, and Zn.

3.3.1. AMD:RM Negative Synergism

(a) Chromium

AMD has a Cr concentration of 34.6 µg/L; on the one hand, RM from Greece leaches out above 18.4 µg/L, and on the other hand, the German releases a concentration 30 times higher (555 µg/L).

The addition of Greek RM in a ratio of 0.1 to AMD favors the precipitation and immobilization of Cr in the mineral phase. For ratios higher than 0.3, this positive effect is only not neutralized but, on the contrary, enhanced to 271 µg/L. AMD in contact with RM.De depicts the same negative behavior, but Cr in the solution is ten times higher than RM.Gr, as shown at Figure 4.

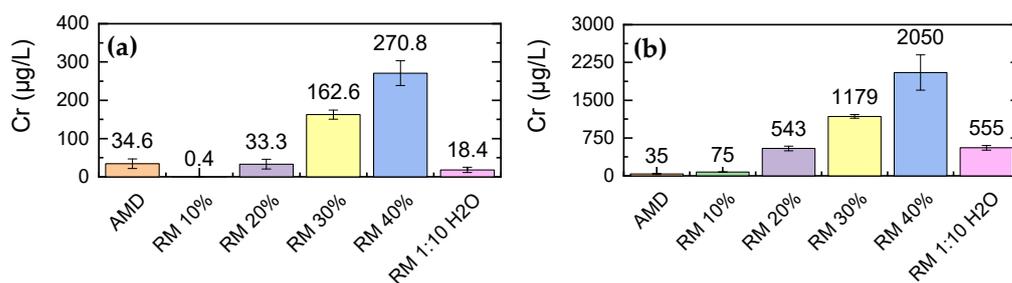


Figure 4. Effect on Cr ions in solution: (a) RM.Gr, and (b) RM.De.

(b) Barium

No leaching of Ba has been seen in both RMs under standard elution tests. Ba concentration in AMD stands at 1.9 µg/L, and despite low concentrations in both solutions (AMD and RM1:10H₂O), mingling both residues had a negative effect when the RM ratio debased 0.3 for Greek and 0.2 for German RM. For a ratio RM/AMD equal to 0.4, Ba in eluates reaches 51 and 77 times its AMD concentration regarding Greek and German RM, respectively (Figure 5).

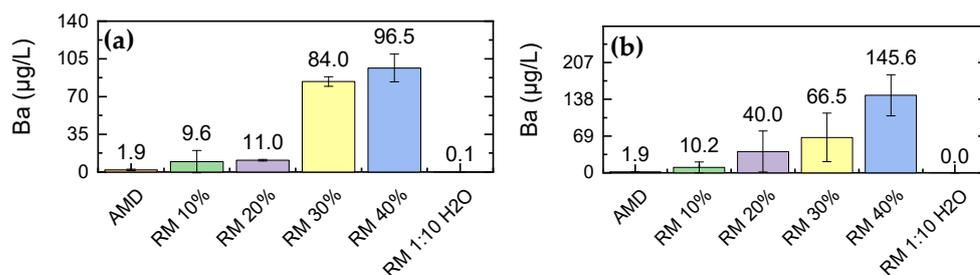


Figure 5. Effect on Ba ions in solution: (a) RM.Gr, and (b) RM.De.

(c) Antimony

As shown in Figure 6, Sb, mainly present in RM, has a concentration well below the limit established for inert waste (0.06 mg/kg or its equivalent in the eluate 600 µg/L). German RM (Figure 6b) tends to increase Sb, but concentrations are still low enough to be considered harmful.

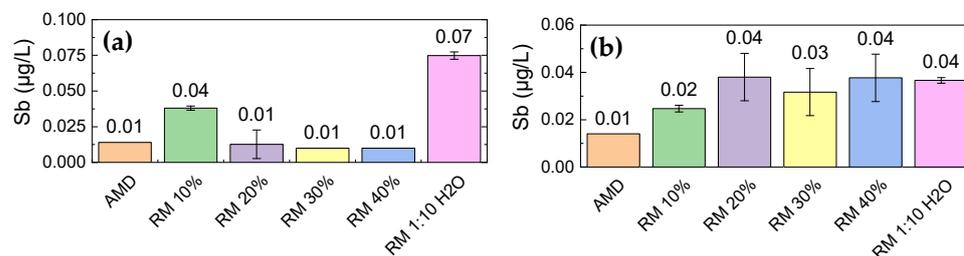


Figure 6. Effect on Sb ions in solution: (a) RM.Gr, and (b) RM.De.

(d) Selenium

Se in RM is leaching out 0.12 mg/kg (12 µg/L in solution) under standard conditions in RM.Gr (Figure 7a) and 0.04 mg/kg (4 µg/L in solution) in RM.De (Figure 7b). In both cases, concentrations are in agreement with the limit of inert waste (see Table 2). AMD enhance the release of Se in harmful concentrations, reaching a maximum of 1005 µg/L in RM.Gr and 82 µg/L in RM.De when the RM ratio is 40%.

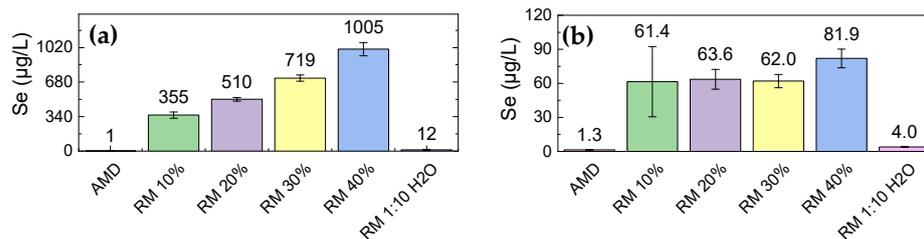


Figure 7. Effect on Se ions in solution: (a) RM.Gr, and (b) RM.De.

3.3.2. AMD:RM Positive Synergism: RM over AMD

Compared to standard leaching conditions, eluates obtained from the two analyzed RM showed Cd, Cu, Pb, and Zn cations within the inert waste limits. RM depicts positive effects on neutralizing these cations from AMD. Regardless, the utilized type of RM, a concentration of 10%, was enough to neutralize Cd, Pb, and Zn almost completely from AMD (see Figures 8–10). The only exception was Cd from RM.De, where a ratio of 0.2 was needed for complete precipitation (Figure 8a).

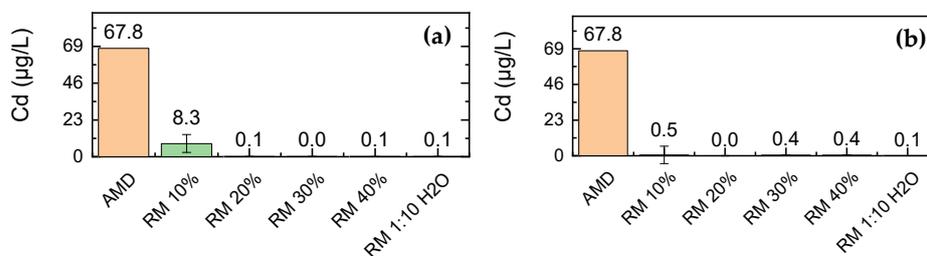


Figure 8. Effect on Cd ions in solution: (a) RM.Gr, and (b) RM.De.

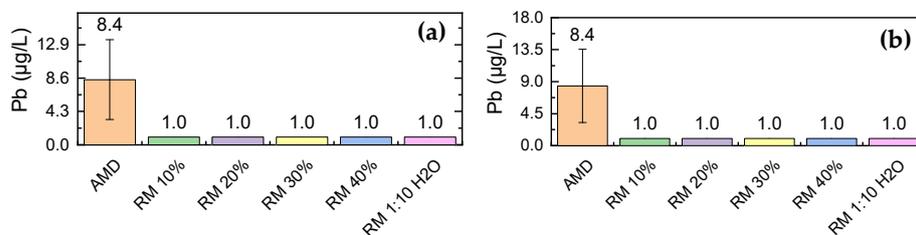


Figure 9. Effect on Pb ions in solution: (a) RM.Gr, and (b) RM.De.

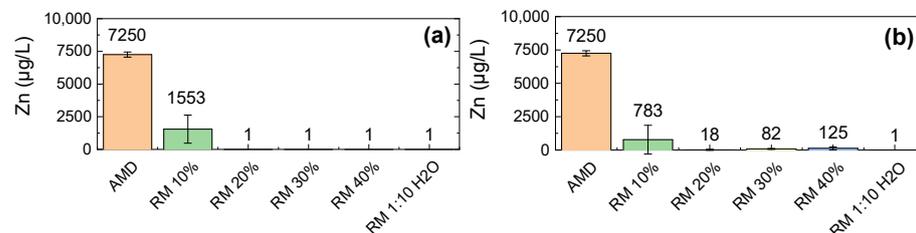


Figure 10. Effect on Zn ions in solution: (a) RM.Gr, and (b) RM.De.

Fe, Cr, Zn, Ni, and Cu are the cations with the higher concentration in AMD, and except Cr, RM is effective in precipitating them. However, perhaps due to its higher alkalinity, German RM is twice as effective as the Greek. This effect is shown in Figure 11 by Ni behavior, where the concentration decreases with increasing RM ratio but at a slower rate using Greek bauxite residues.

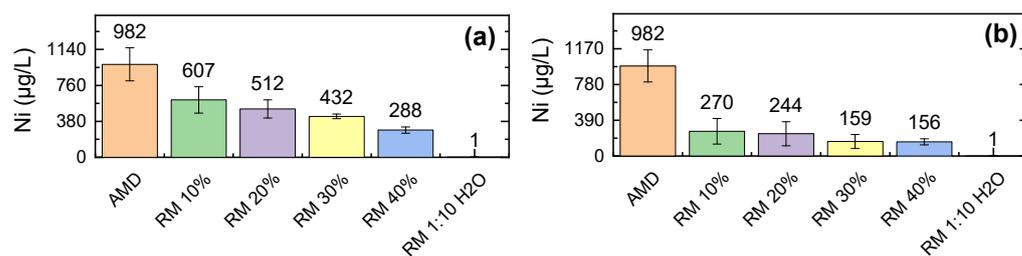


Figure 11. Effect on Ni ions in solution: (a) RM.Gr, and (b) RM.De.

An RM ratio of 0.1 showed to be adequate to precipitate Cu, but increasing the ratio beyond 0.1 decreases the RM efficiency to neutralize Cu cations from AMD (see Figure 12).

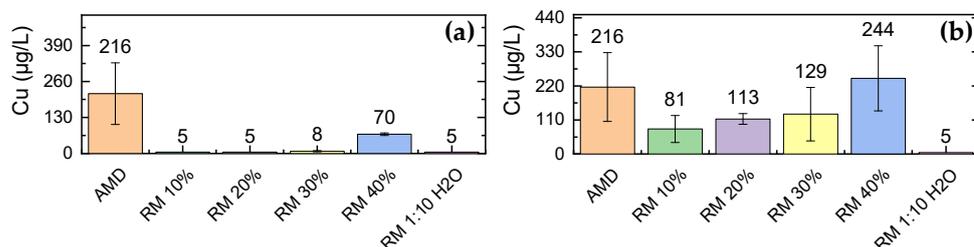


Figure 12. Effect on Cu ions in solution: (a) RM.Gr, and (b) RM.De.

For an RM ratio of 0.4, the eluate contains 244 µg/L in RM.De against 70 µg/L when Greek RM is utilized.

Besides its higher alkalinity, RM also contains elements outside the established limits to be considered an inert waste. Standard elution tests showed that As leaches out 3.9 mg/kg (389 µg/L) in RM.Gr and 0.07 mg/kg (6.7 µg/L) in RM.De (see Tables 1 and 2). According to these results, Greek RM releases As under the limits of non-hazardous waste and the German below the limits of inert waste (see limits in Table 2). AMD also contains As (13 µg/L) but in a concentration that cannot be considered harmful. In both cases, RM proved to be effective to immobilize As in the mineral phase (see Figure 13).

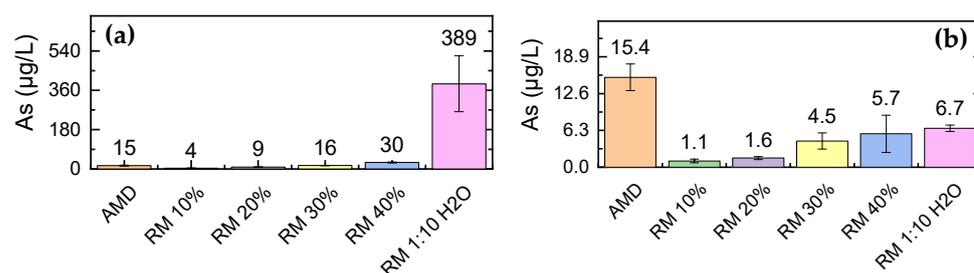


Figure 13. Effect on As ions in solution: (a) RM.Gr, and (b) RM.De.

Mo concentration in AMD is extremely low but is naturally leaching out from RM in contact with distilled water. Greek RM releases around 200 times more Mo than the German (Figure 14); nevertheless, both were underneath the limit of 0.5 mg/kg for inert waste (see Table 2).

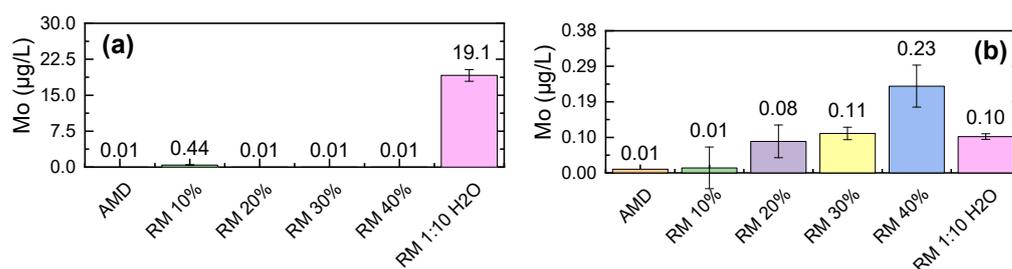


Figure 14. Effect on Mo ions in solution: (a) RM.Gr, and (b) RM.De.

For RM ratios higher than 0.1, AMD fully immobilizes Mo. In German RM, Mo's solubility increased with the RM ratio; nevertheless, the concentration was still below 50 µg/L to be considered outside the inert waste limits (see Table 2).

Vanadium (V) as a critical metal is not officially included in the list of chemical elements present in waste that have to be monitored to decide its classification and treatment. Nevertheless, studies have demonstrated associations between V and an increased risk of several pathologies like hypertension, dysrhythmia, and cancer, besides other health risks [20]. According to the standard EN 12457-2, V in RM leached out 2.6 and 0.2 mg/L in Greek and German RM, respectively. Di Carlo et al. [21] showed that the V release in RM is outside phytotoxic levels representing a risk to the environment. Like As behavior, AMD favors neutralization and immobilization of V in the RM mineral phase (as shown in Figure 15).

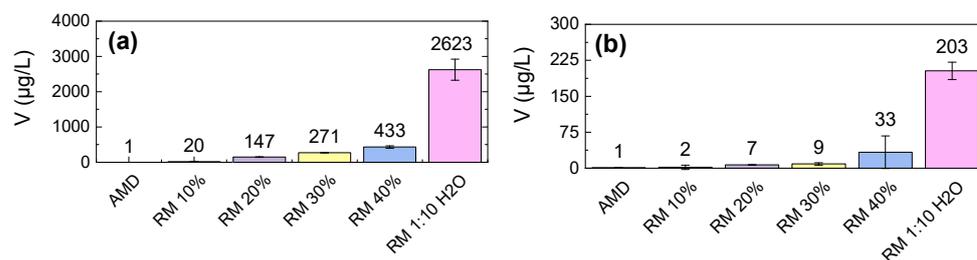


Figure 15. Effect on V ions in solution: (a) RM.Gr, and (b) RM.De.

3.4. Discussion of Concentration of Elements in the Mineral Phase

Fe and S were the main elements in AMD, and tend to precipitate in the mineral phase when pH increases by adding RM (see Table 4). Before mixing both residue types, Fe-oxide represented 46 wt% and 32 wt% in Greek and German RMs, respectively. Nevertheless, these concentrations rise to 50 wt% for the Greek and 31.4 wt% for the German when the RM ratio goes to 0.4. The starting S content in RM is 0.1% in Greek and 0.04% in German RM. These concentrations reach a maximum of 3.4% in RM.Gr and 1.5% in RM.De for an RM ratio of 0.1.

As shown in Figure 16, Ni is slightly enriched in RM when the higher ratio is utilized to neutralize AMD. These results are also consistent with Ni's decreasing profile in the eluates (as shown previously in Figure 12). Figure 16b shows a constant V concentration in the German RM and a slight decrease in the Greek for RM ratios 0.1 and 0.2. As shown in Figure 16, there is almost no V in AMD, and this element is immobilized in RM when AMD reacts with it. Therefore, the decrease of Ni is explained by the precipitation of other elements such as S and Fe.

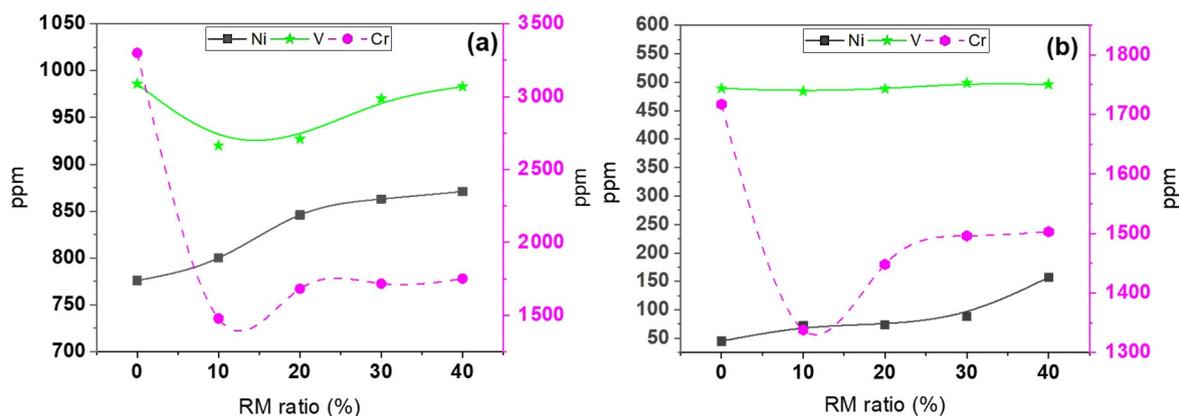


Figure 16. Concentration of Ni, V, Zn in the mineral phase: (a) Greek RM and (b) German RM.

Cr was one of the few exceptions in the synergistic approach of mixing AMD and RM. Cr content diminishes in both RMs (Figure 16) while increasing in the eluates (Figure 5). Besides the negative environmental impact of releasing Cr in the eluates, the selectivity with which this element is released while most of the other components precipitate allows us to imagine a method to recover Cr from RM.

Figure 17 shows the impact of mixing AMD with RM for several strategic and valuable metals such as Y, La, Ce, Nd, and Nb. For Y, La, and Nb, no significant change has been seen in their concentration when the RM ratio increases. Nd has a smooth decline compared with the original content in RM. On the other hand, Ce shows a marked increase in the mineral phase of both RMs, suggesting that this element was present in AMD.

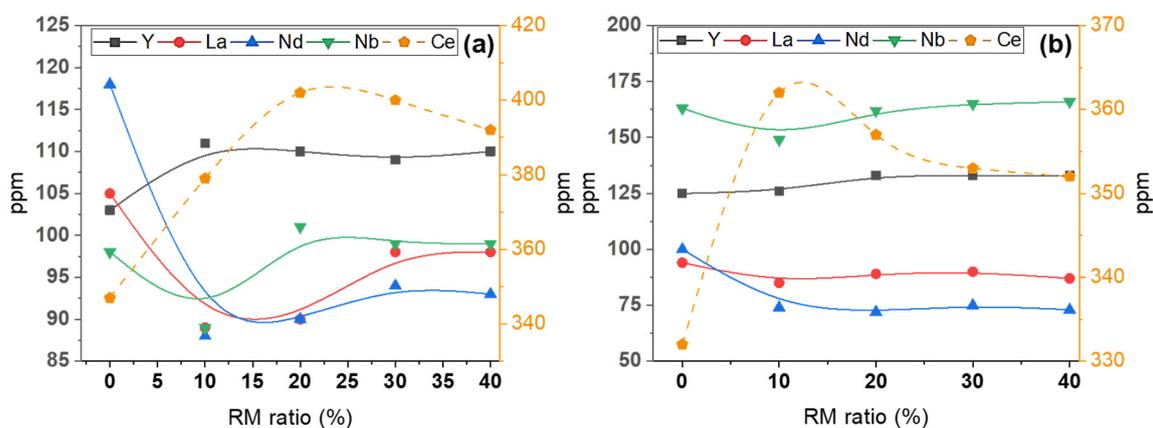


Figure 17. Concentration of Y, La, Nd, Nb, and Ce in the mineral phase: (a) Greek RM and (b) German RM.

4. Conclusions

The following conclusions are found in this work:

- AMD has benefited from RM's alkaline character, favoring a complete immobilization of fluoride ions and a substantial reduction of sulfates. Nevertheless, the decrease of sulfates was not enough to reach a concentration of 5 g/L, which is the limit for not being considered hazardous according to the EU Landfill Directive 1999/31/EC.
- NO₃ concentration by using Greek or German RM to neutralize AMD showed different trends, and these results should be deeply studied, especially the interaction of AMD microbial communities with RM.
- There is a net positive synergism on mixing an alkaline waste such as RM with AMD from an environmental perspective. RM over AMD was efficient to neutralize Cd, Pb,

Ni, Cu, and Zn. On the other hand, AMD was effective to immobilize As, Mo, and V from RM.

- Regarding Cr, Ba, Se, and Sb, the mix offers selective separation despite a negative increment of these ions in the eluates. Nevertheless, Ba and Sb's increments were low compared to legally established limits to consider waste as harmful. The selective dissolution of Cr and the immobilization of most of the metallic ions in the mineral phase can be a strategy to explore in order to recover this element.
- Valuable elements present in RM such as La, Nd, and Nb tend to remain in the mineral phase. Elements such as Ce and Y present in AMD precipitates under the effect of RM enriching the mineral phase. Several authors had explored a pyrometallurgical treatment of RM to recover pig iron and enhance the content of critical raw material (CRM) in the final slag [22–24]. This approach can be beneficial to increase both pig iron and CRM from the filter cakes produce after coagulating AMD ions into an RM matrix.
- Except for an increase of Cr in solution, both RM showed a positive net effect in decreasing and immobilizing the primary metal ions considered hazardous to human life and ecosystems. M. Cvijovic et al. [25] proposed improved chemical treatment of surface water and sludge application as a compost. As shown in their work, the metals with content over the maximum limit (mg/kg), 169 Ni, 69 Cr, and 5.7 Pb, can be reduced by zeolite, which is maybe a solution for removal of Cr from our solution.

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