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MINE SOLID RESIDUE AND MINE WATER TREATMENT AT LABORATORY AND PILOT SCALE BY MODIFIED BAUXITE RESIDUE WITH GYPSUM, AN EFFECTIVE AND CHEAP SOURCE OF IRON AND ALKALINITY

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SUMMARY: Immobilisation of trace elements from mine residues, contaminated soils and water is effective with modified bauxite residue (MBR). The red mud from alumina production is washed and dried in press-filter, and reacted with gypsum to lower the pH from 11.5-10.5 to 8.5 (about the pH of limestone in water), and that non-hazardous waste reacts with elements, due to the reactive iron and aluminium oxyhydroxides and the alkalinity content. Laboratory treatment of 5 mine pyritic residues, one sub-soil and 9 mine waters are presented. Abatement is for most element and sample > 99%. A small plot treatment of mine residue (2*30 m²) and a pilot treatment of water (3000 l) were successful.

For mine residue, the dose of MBR can be adjusted until the leachable fraction of trace elements is below the European inert landfill acceptance criteria. At that dose, with mineral fertilizers at agronomic rate for oligotrophic soils, normal plant growth of common species is obtained. For pyritic residues, MBR input should be related to the acid-gererating capacity of the mine residue. The modified bauxite residue can decontaminate heavily polluted mine water, and the preliminary results from lysimeters and speciation study indicate that the immobilization could be stable.

Hypothesis for mechanisms of immobilization of elements are presented (Fe and Al: surface precipitation by effect of pH; Zn and Cd: complexation by oxihydroxides of Fe and Al, electrostatic attraction is probably secondary; As: inner-sphere complex; Fe: oxidation and Mn: oxidation accelerated by a pH effect and a surface effect of Mn (II) to Mn (IV) and precipitation as MnO_2).

1. INTRODUCTION

The lack of efficient and sustainable remediation technologies has led to either an improper or a complete lack of management of trace-elements-contaminated soils for decades. As a result,

soil contaminants continue to spread to surface water, groundwater, and the food chain, thereby increasing ecosystem and human exposure to hazardous trace elements (TE) (Kumpiene *et al.* 2014). Phytoremediation can be used for TE-contaminated soils. It uses plants and associated microorganisms to remove (phytoextraction) or stabilize TEs (phytostabilization), eventually assisted by soil amendments. Researches focus on chemical tests to assess the phytotoxic fraction of TE, biological tests to assess the remaining toxicity, and amendment efficiency (i.e. Mench *et al.* 2009). Amendments are iron scraps or grits (oxidized or at zero oxidation state), alkaline wastes (like ashes), clay, lime, limestone, and organic matter (manure, sewage sludge, biosolids, compost…). Amendment is used in limited amounts, typically at 1% by soil weight for iron, to up to 5 % for organic matter (corresponding to an approximate mass of 250 tons/hectare with 0.3 m depth and soil density of 1500 kg/m^3), or even up to 50 % in mine spoils. Most of the time, phytotoxicity is reduced but not cancelled, and hence precise test for remaining extractable TE correlated with biological tests responses is a field of work. Another approach is proposed here: use of an amendment until the abatement of leaching TE at the level of the European inert landfill acceptance criteria is obtained (leaching with DI water according to waste method EN 12457-2). Further trials (not shown here) with pyritic residues indicate that MBR input should be related to the acid-gererating capacity of the mine residue.

The capacity of fixation of trace elements (TE) of contaminated <u>water</u> by bauxite residue is well established at the laboratory (i.e. Collins 2014). Nevertheless the pH of treated water with raw red mud can be high, and the new waste that is produced (the spent red mud) must be managed. Laboratory immobilization of elements from 9 mine waters at equilibrium, and some kinetics are produced. This study uses granulated modified bauxite residue (MBR) at pH 8.5 for treatment of acid mine water at laboratory scale and at pilot scale (50 kg of MBR and 1500 l of water in two repetitions). Preliminary results of the long-term behavior of the MBR after the water treatment (the spent MBR) with waste leaching test (EN 12457-2), with lysimeters and with a geochemical speciation approach show that the stabilization of the TE could be strong enough to store the spent MBR at the abandoned former mining sites.

2. MATERIAL AND METHODS

2.1 Rationale for use of Modified Bauxite Residue (MBR)

From a geochemical point of view, the mechanisms involved in element fixation in water and soils are TE complexation (by input of complexing minerals and/or organic matter: clay, iron scraps or grits oxidized or at zero oxidation state and oxidizing in the soil, organic manure, sewage sludge, compost…) and TE precipitation (by input of alkalinity: lime, limestone, alkaline waste, ashes...). Applied rates are limited: iron grit is expensive, and the production of dissolved organic matter must be avoided. If the input of organic matter exceeds the capacity of the microbial community to mineralize the dissolved organic carbon generated by the organic matter decay, colloidal dissolved organic matter will move with the leaching water and mobilize TE to the ground water.

The use of modified bauxite residue (MBR) could bring a solution. The red mud from alumina production is washed and dried in press-filter, and reacted with gypsum to lower the pH from 10.5 to 8.5 (about the pH of limestone in water) (pH at L/S 10 l/kg 24 h according to EN 12457-2). If nutrients are added, the plants grow in this non-hazardous waste. The iron content of MBR is 34.9 %. The capacity of complexation is high: tests with contaminated water from mine sites have shown that MBR can fix 5 g of Zn per kg. The alkalinity of MBR is 2.72, 2.09, 1.45 and 0.48 mol OH$^-$/kg from pH 8.5 to pH 5, 6, 7 and 8 respectively. The iron of MBR is 30 times

less expensive per kg than iron grit alone, without taking into account the input of alkalinity. Since MBR is less concentrated in iron than iron grit, long transport (hundreds of km) costs will reduce the advantage of MBR. An additional advantage is the use of a waste to treat wastes, without consuming additional non renewable resources, a requirement for a circular economy.

2.2 Mining residue, soil and water data

Mining residue from three different locations with pyritic ores, abandoned for decades, was sampled. A sub-soil of the city of Marseille was also used. Mine water from different locations and different quality (acid mine water, neutral mine water, run-off and neutral mine water, and neutral mine water specially rich in Mn) were sampled.

2.3 Treatments

The mining residues or soil are mixed with the modified bauxite residue and allow reacting for 4 weeks, with moisture content at water holding capacity. The samples are then leached (EN 12457-2, 10 l/kg). The waters are mixed with bauxite residue or modified bauxite residue in flasks, and allow reacting for 4 days. The supernatant is filtered and analysed.

A field trial of mining residue treatment was implemented. At spring 2014, two plots of 30 m² were terraced and leveled and the stones removed. RBM was added in a plot at 30 kg/m² and the two plots were tilled and mixed up to 30 cm deep. After one month, the soil received fertilizer (N-P_2O_5-K_2O 133-80-133 kg / ha) and seed of a common grass (*Dactylis glomerata*) and legume (*Onobrychis sativa*).

A pilot treatment of water was implemented, with granulated MBR.

3. RESULTS

3.1 Mine residue and soil

An example of the effect of the dose of the MBR on the leachable concentration of elements at the laboratory is presented at Figure 1. This soil has a huge amount of leaching TE and no vegetation growth since the abandonment of the mine. An input of 10% of MBR reduces the leaching concentration below the European landfill acceptance criteria for inert wastes. Results with 5 mine soils and the excavated sib-soil and sediments are presented at Table 1.
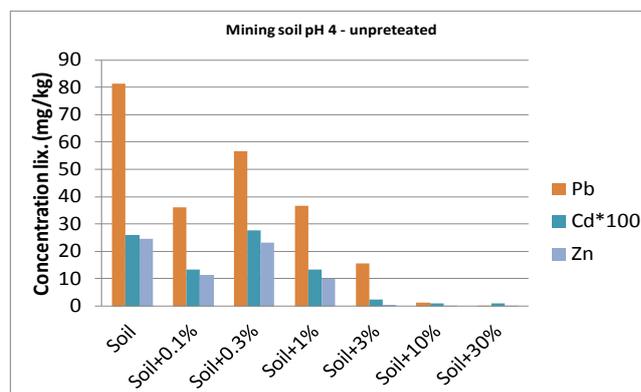
Figure 1: TE leaching concentration of mine residue RMA1-1 treated with modified bauxite residue (0.1% to 30% of the mine residue+MBR mixture)

Table 1. Dose of modified bauxite residue, initial and final pH, and ratio of leachable elements after and before the treatment on 5 mine residues and a sub-soil (the ratio is underlined when the final leachable concentration is below the LOQ)

Residue/Soil	Dose	pH initial	pH final	Pb	Zn	Cd	Cu	Ni	As	Mn	Cr	Mo	Se
RMA3-1	10% + CaCO3 eq. to actual acidity	2.43	6.51	0.1095			0.0010	0.0672	0.0645		0.1519	1.5	
RMA3-2	3%	2.55	4.89	0.3873			0.0113				0.9	0.9	
RMA2	1%	3.50	6.50	0.3427	0.0203					0.1498	1	1	
RMA1-1	10%	3.54	7.08	0.0159	0.0008	0.0385					1	1	1
RMA1-2	10%	6.80	7.60	0.0222	0.0052	0.0048					1	1	2
Sub-soil Marseille	0.10%	7.74	6.95	0.6000				0.0714			0.0606	0.9	1

Since oxidation of sulphides is active in the pyritic mine residue, the amount of alkalinity is in the present trials adapted to the acid generation potential of the samples.

The leached quantities of elements in lysimeters in Aix-en-Provence from mine residue RMA1-1 during one year are presented at Figure 2. The decrease of emission of the treated mine residue (Soil+MBR) is for lead 12 times, for cadmium 45 times and for zinc is 352 times, compared to untreated MBR (Soil).
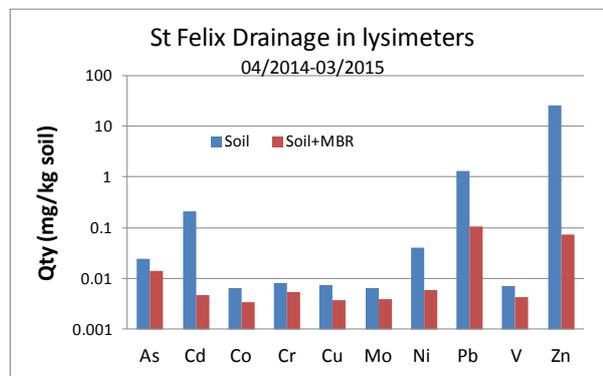

Figure 2: Cumulative emission of trace elements of a pyritic mining residue not treated (soil) and treated (soil + MBR) in lysimeters during one year

The result of the field trial is presented at Figure 3. The control plot has no vegetation and the treated plot is floroushing.

Figure 3: Use of MBR at pilot scale and vegetation 216 days after seeming

3.2 Water treatment

Results of treatment at the laboratory of 9 natural waters sorted by increasing pH are presented at Table 2. When the ration of final/initial concentration is > 0.01, the ratio is colored in yellow. When the LOQ is obtained, the ratio is underlined.

Table 2: Initial and final pH, dose of modified bauxite residue (L/S = liter of water per kg of MBR) and ratio of leachable elements after and before the treatment on 9 water (AMD= acid mine drainage, NMD= neutral mine drainage, RNMD= runoff and neutral mine drainage)

Water	pHi	pHf	L/S	Mn f/i	As f/i	Cd f/i	Cu f/i	Ni f/i	Pb f/i	Zn f/i	Cr f/i	Cr f	Mo f/i	Se f/i
AMD	2.7	8.0	20	0.001		0.001	0.016	0.036	0.019	0.0004	2.1	0.104	1.8	1.0
AMD	3.3	9.0	21	0.001	0.0001	0.077	0.010	0.032	0.008	0.001	1.2	0.043	2.8	2.0
AMD	3.5	7.0	300	0.047		0.217			0.079	0.006	1.2	0.006	1.0	1.0
AMD	3.9	8.5	30	0.001	0.063	0.041	0.0004	0.015		0.008	4.0	0.020	1.0	1.0
NMD	6.3	8.3	100			0.018		0.102		0.002	5.4	0.027	1.0	1.0
NMD-Mn	6.3	8.2	50	0.001							13.4	0.067	1.6	0.5
NMD	6.7	8.5	6.77		0.033					0.024	6.4	0.051	1.8	1.0
RNMD	7.7	8.0	30	0.008	0.065						7.9	0.040	1.2	1.0
RNMD	8.0	8.4	30	0.004	0.053						8.8	0.044	1.1	1.0
Cc i max (mg/l)				58.0	57.6	4.55	26.5	3.24	1.05	130	0.049		0.032	0.030
Cc f max (mg/l)				0.065	1.39	0.005	0.010	0.050	0.008	0.090	0.104		0.036	0.030

The kinetic of immobilization have been measured for some elements. The time to immobilize 90% of the concentration and the hypothesized mechanisms are:
- Fe, Al: < 1 min (oxidation, precipitation)
- Zn: 26 min, Cd : 32 min (non-specific complexation by Fe and Al oxyhydroxydes);
- Mn: 38 min (oxidation and precipitation accelerated by MnO_2);
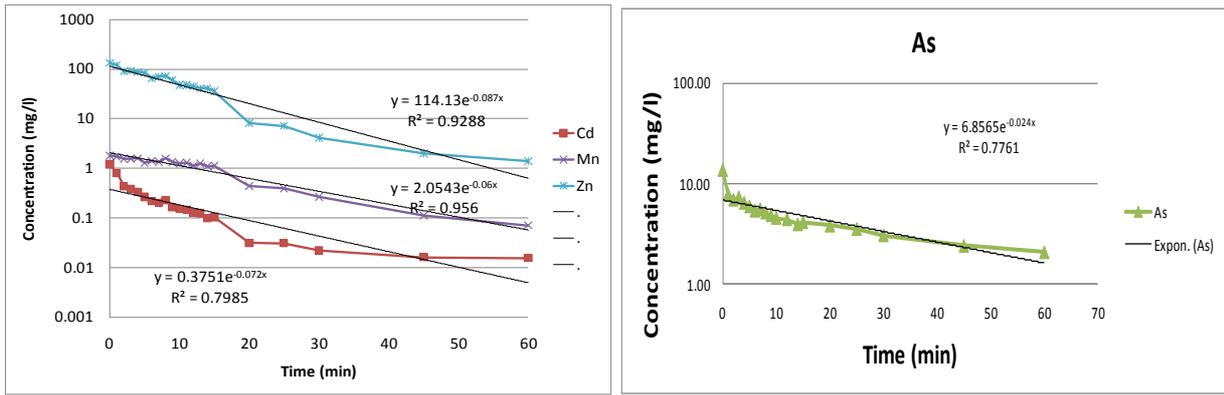- As: 96 min (specific complexation by Fe and Al oxyhydroxydes).

Figure 4: Kinetic of immobilisation for some elements

For the pilot treatment of water, the MBR has been granulated in pellets with a diameter of 2 mm (Figure 5). Laboratory trials with an acid mine drainage (AMD) water of St Felix (pH 4.5, 132 mg Zn/l and 1.21 mg Cd/l, rich in Al and Fe) have shown successful fixation at a L/S ratio of 30 l water / kg MBR with a first order kinetic and a time to reduce the concentration of 90% of 32 min for Cd and 26 min for Zn. The residence time of the water in the pilot was hence set to 1 h. A volume of 1500 l of St Felix water were pumped into a tank filled with 50 kg of granulated MBR during 3 days (Figure 5). The test was repeated. Water was analyzed and the used RBM is tested for leaching and lysimeters emission, and TE speciation. The abatement was of 99.03% Zn and Cd (Figure 6).

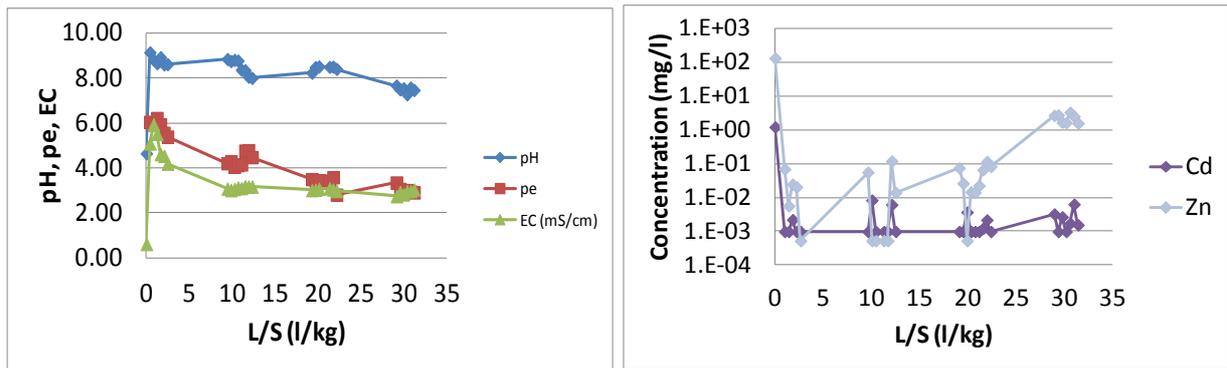Figure 5: Granulated MBR, and water treatment at pilot scale

Figure 6: pH, redox potential (pe) and electric conductivity of the water at the outlet of the pilot, and concentration of Cd and Zn at the outlet of the pilot (initial concentration 132 mg Zn/l and 1.21 mg Cd/l).

3.3 Long-term behaviour of spent MBR

The leaching concentrations of TE from the spent MBR are all below the European landfill acceptance criteria for inert waste. The spent MBR is studied in lysimeters (Figure 7) with different top layers, simulating different options for storage (top layer of sand, unused MBR, vegetated MBR and natural soil) for some years. There are no differences in emission between the MBR that has not treated water, and the used-MBR (Figure 8). The top layer reduces the amount of percolating water, and the emissions are reduced by a factor of 10 with a vegetated soil, in comparison with a cover of sand or un-vegetated MBR.

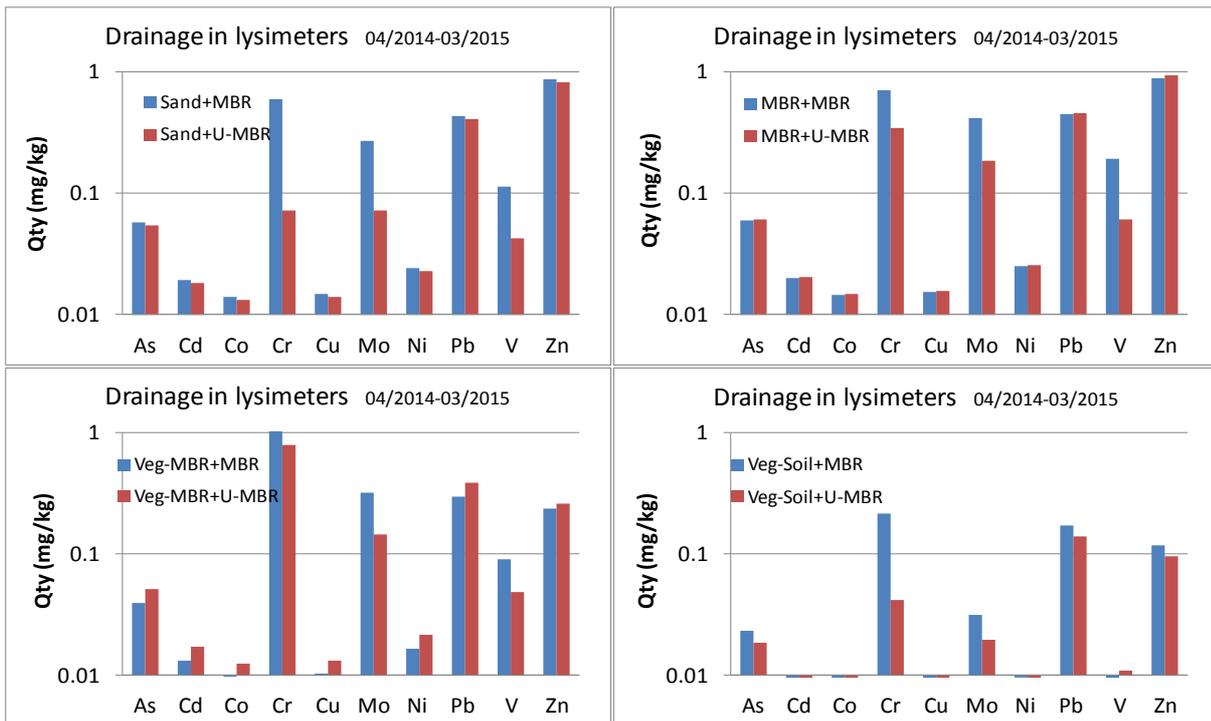Figure 7: Lysimeters of spent MBR with different top layer

Figure 8: Emission of trace elements from MBR not used for water treatment (MBR) and after water treatment (U-MBR), with different top layer (sand, MBR, vegetated MBR, and vegetated soil).

The speciation of Zn in the spent MBR (Figure 9) shows that at pH 8.5, the Zn is fixed to 99.985% by the oxihydroxides of Fe and Al. In the Figure, "DOC-bound" is the Zn fraction associated with organic matter in solution, and "POM-bound" is the Zn fraction associated with organic matter. As long as neither acidification nor reduction of these oxides occurs, the Zn should be stabilized. The results are consistent with Collins *et al* 2014. This work has been done in collaboration with J. Dijkstra and A. van Zomeren, Energy Center of the Netherlands. According to the experimental results of water treatment and literature, attachment mechanisms are probably:

- Surface precipitation (Fe and Al) by effect of pH
- Complexation oxihydroxides of Fe and Al (Zn and Cd) (electrostatic attraction is secondary)
- Specific complexing internal sphere moving towards a covalent bond (As).
- Oxidation (Fe) and accelerated by the surface oxidation and pH effect of Mn (II) to Mn (IV) and precipitation of MnO2
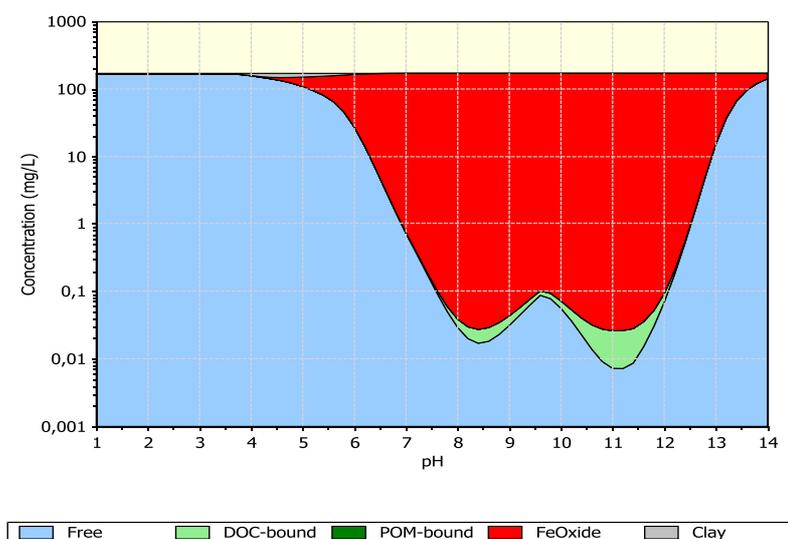
Figure 9: Speciation of Zn in spent MBR and in solution (Free = Zn in solution, DOC-bound = Zn complexed by dissolved organic carbon in solution, POM-bound = Zn complexed by particulate organic matter, FeOxide = Zn adsorbed/complexed by reactive Fe and Al oxihydroxides, Clay = Zn non-specific adsorbed on clay)

5. CONCLUSIONS

Modified bauxite residue brings reactive iron (complexing trace elements) and alkalinity buffered at pH 8.5 (precipitating trace elements). For mine residue, the dose of input can be adjusted until the leachable fraction of trace elements is below the European inert landfill acceptance criteria. At that dose, with mineral fertilizers at agronomic rate for oligotrophic soils, normal plant growth of common species is obtained. The modified bauxite residue can decontaminate heavily polluted mine water, and the preliminary results from lysimeters and speciation study indicate that the immobilization could be stable.

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