REMTECH Europe

# GOING WITH THE GEOCHEMICAL CYCLE

## ENVIRONMENTAL REHABILITATION WITH MINERALS USING GEOCHEMICAL TECHNOLOGY

Alberto Angeloni | Montana & Hans Zijlstra | GeoChemTec @ Virtual RemTech 2020

Montana GeoChemTec

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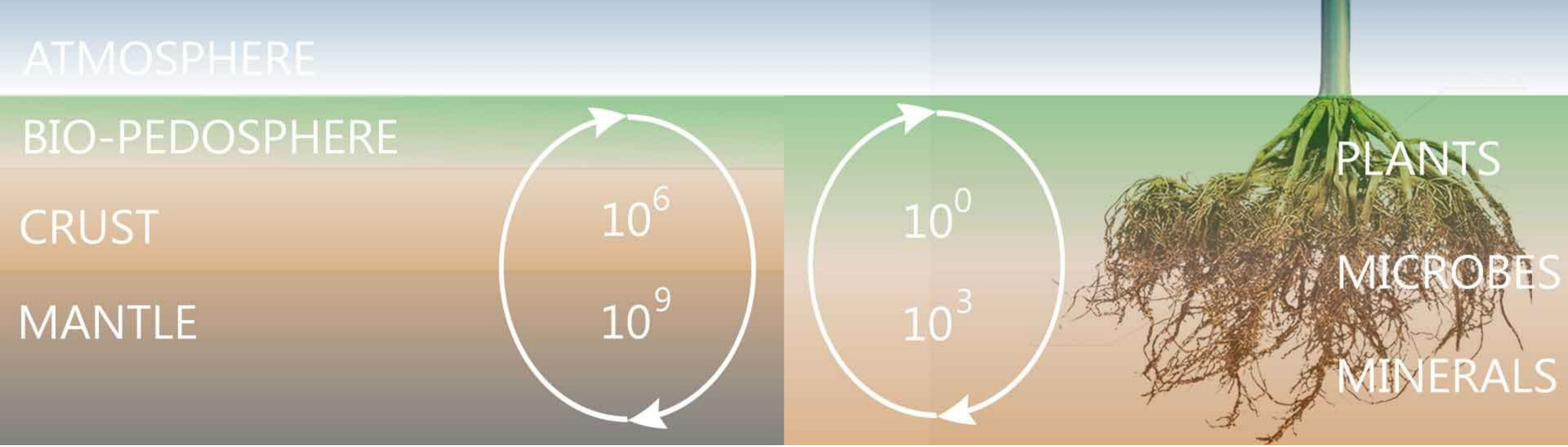



# INTRODUCTION

**Geochemical cycle**

Geochemical technology

Mining waste management

# GEOCHEMICAL CYCLE

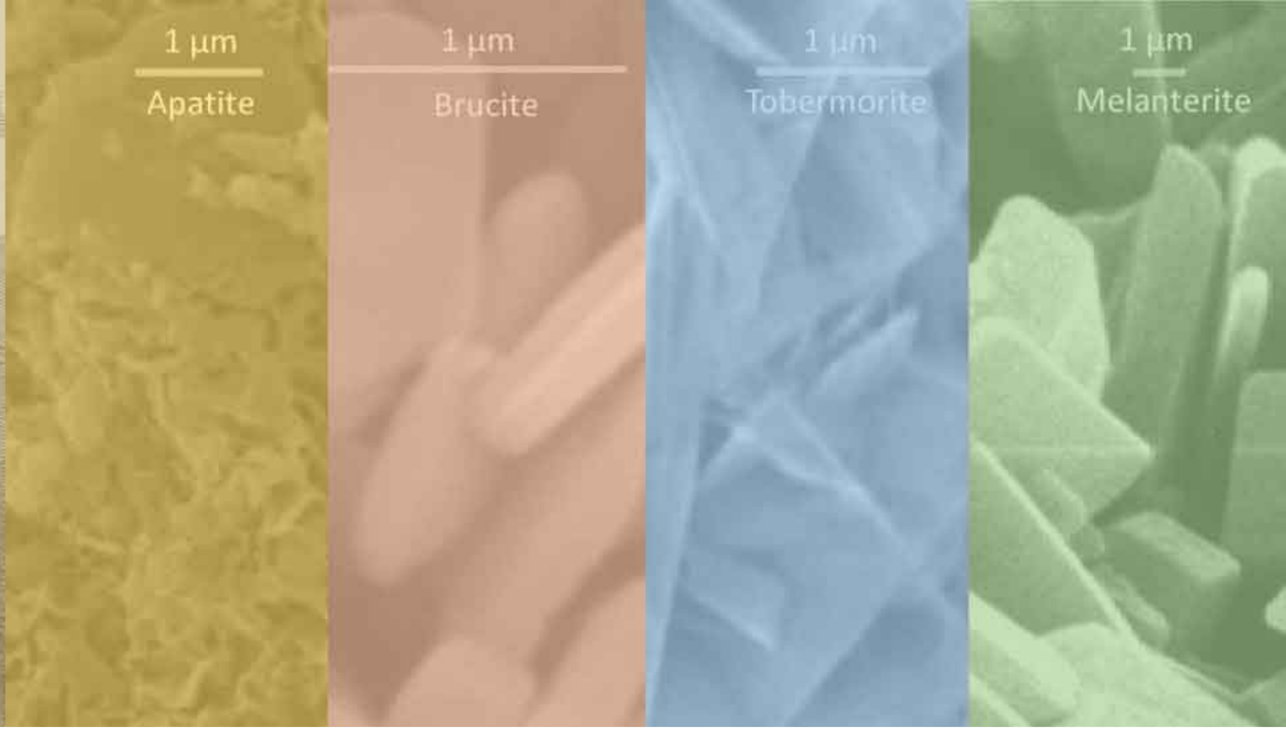
Hazardous compounds in the open natural environment, such as heavy metals, are part of geochemical cycles.

*Long cycles* - follow continental drift.

For instance, heavy metals concentrate in the lithosphere as ores, are brought to the surface, weather, disperse, are deposited, get buried and concentrate again to complete a long cycle of millions to billions of years.

*Short cycles* - operate in soil, were minerals are bio-weathered by microbes around plant roots.

Here, heavy metals are released into groundwater, disperse, adsorb, precipitate, and concentrate again as minerals, completing a short cycle of years to millennia.




# INTRODUCTION

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# GEOCHEMICAL TECHNOLOGY

Geochemical technology is conceived after studying geochemical cycles and natural examples of reactive transport, involving dilution, transformation, concentration, immobilization, and isolation.

Geochemical technology is not new.

Hannibal may already have used geochemical technology, when making fire and pouring vinegar on limestone rocks, splitting them to secure a passage over the Alps, on his way to Rome.

We think that with geochemical technology, one can better manage the natural environment, keeping bioavailable heavy metals within natural background concentrations and reach maximum geo- and biodiversity.

Geochemical technology works with minerals and uses preferentially passive treatment, without industrial installations, power, or continuous supervision, for better blending into the natural environment

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# MINING WASTE MANAGEMENT

In the Mediterranean countries, many abandoned historical mines pollute the environment with heavy metals.

Current Best Available Technologies for mining waste management in remote, semi-arid, mountainous areas are:

For *waste-rock*, onsite isolation in disposal sites with impermeable layers of geotextile, clay, and plastic, that must withstand torrentuous weather and the dynamics of strong relief and.

For *waste-water*, passive treatment, using compact, highly efficient, mineral filters.

# WASTE TO WASTE

**Neutralize 70 million m3 acid mining waste with 20 million m3 alkaline red mud**

Transform caustic bauxite refinery residue with solar salt plant brine

Earn €100/t treatment, €300/t arsenate removal, €1500/t electrokinesis

# NEUTRALIZE ACID MINING WASTE WITH ALKALINE RED MUD

For instance, on the island of Sardinia, in the western Mediterranean, there are at least 70 million m3 of acid mining waste with heavy metals, that need treatment.

There is also a bauxite refinery that produced 20 million m3 of caustic red mud of very-fine ground iron (hydr) oxides and alkaline sodium minerals.

Ing. Antonio Zucca showed that by mixing both we can produce neutral soil, wherein the heavy metals are immobilized on the long term.

This is a waste to waste geochemical technology, serving better management of both mining- and processing waste.

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# TRANSFORM BAUXITE REFINERY RESIDUE WITH SALT PLANT BRINE

Good geochemical technology works slowly, so that few stable minerals can form, instead of many small unstable ones, with high specific surface in watery sludge.

Therefore, the very caustic red mud needs first to be mixed with seawater as shown by Prof David McConchie, or with local solar salt plant brine as done by Virotec Italia.

Doing so, will transform the very soluble and reactive sodium minerals into much less soluble, slower reacting calcium and magnesium minerals.

The pH drops then from 13 to around 8.5, while the alkalinity and acid neutralizing capacity decreases only slightly, from 4.5 to 4.2 moles of hydrogen per kg of red mud.

The transformed red mud slurry is then further processed into powders for mixing and into porous cemented granules for filtration.

Three case studies serve as an example of the efficiency and economic viability of geochemical technology, when using, for instance, transformed red mud.


| | ViroMine™ g/L | pH | Cu mg/L | Fe mg/L | Zn mg/L | $SO_4$ mg/L |
|---|---|---|---|---|---|---|
| Raw | - | 2.0 | 933 | 14461 | 1962 | 65640 |
| Treated | 44 | 8.2 | <1 | 7 | <1 | 68913 |

# WASTE TO WASTE

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# EARN €100/T TREATMENT

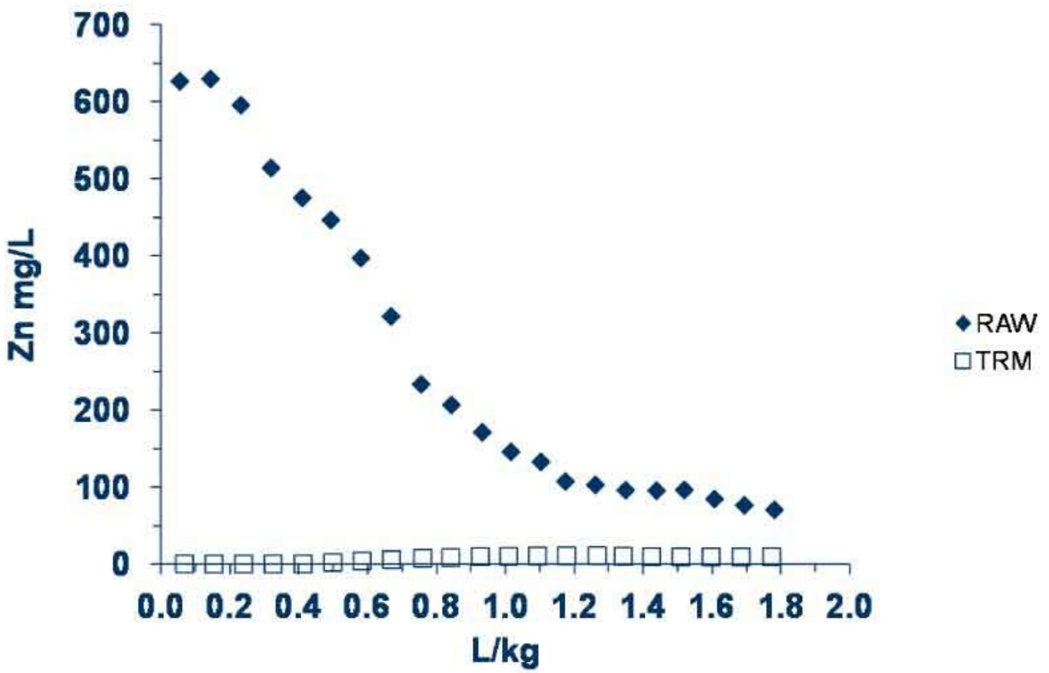
The first case concerns the mixing of powder with the extremely contaminated Aqua Forte water, concentrated by evaporation, in a tailings pond of a dormant zinc mine, at Aljustrel in Portugal.

Because of the very high concentrations of heavy metals, fast reacting lime turned the water into a gel and it produced very voluminous sludge.

This was not the case when the water was pumped up, mixed with the much slower reacting minerals of transformed red mud, and then sprayed back over the pond.

The fine-grained, high density particles of the transformed red mud captured the heavy metals in their alkaline boundary layers, while settling slowly into a stable bottom layer, that could be left in place, after the supernatant water was discharged.

In this case, apart from transport costs, charging €100/ton of transformed red mud powder proved to be economically viable.

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# €300/T ARSENATE REMOVAL

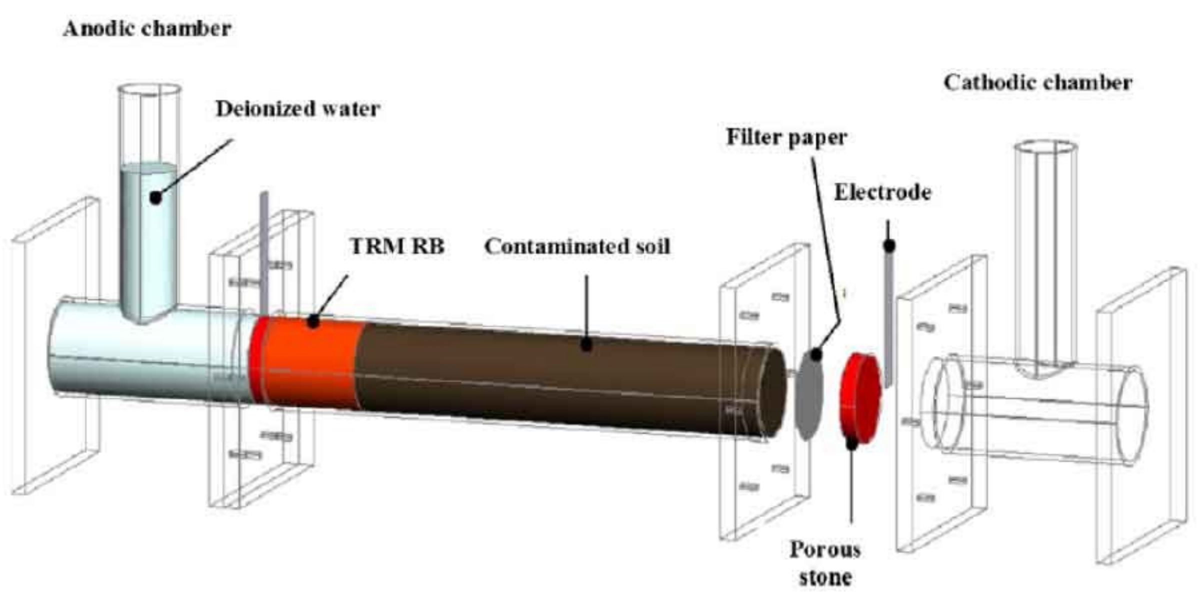
In the second case, we used porous cemented granules of transformed red mud.

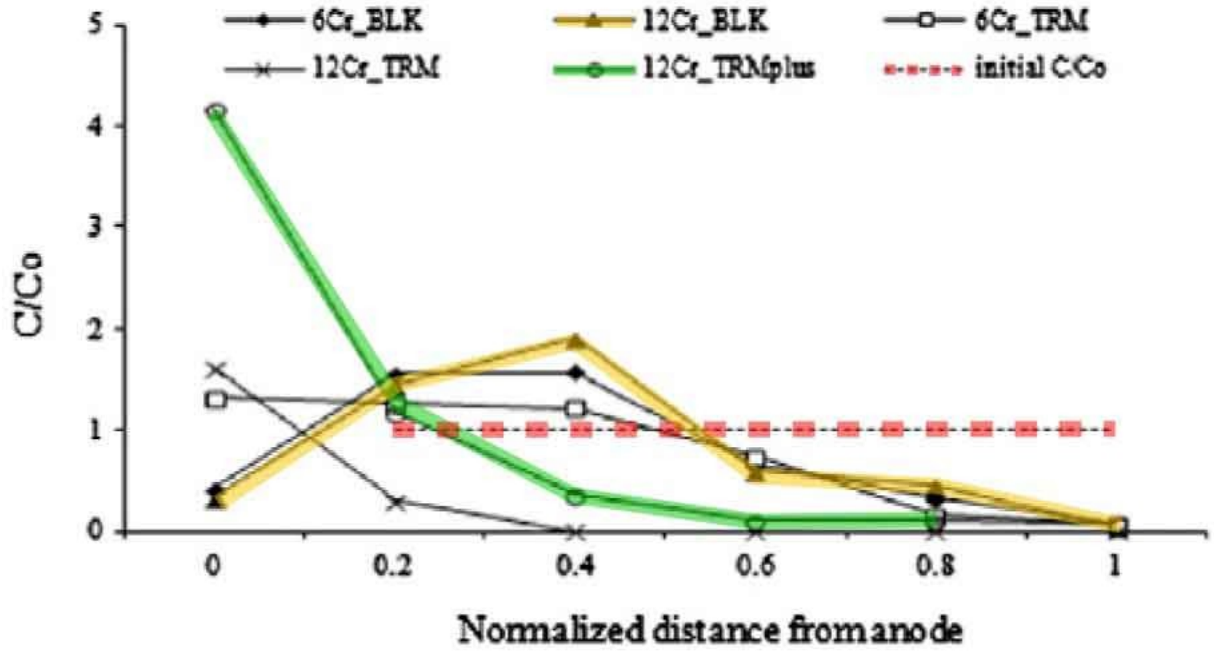
Placed in a bed below waste rock from the abandoned lead arsenic sulfide mine of Baccu Locci, near the town of Villaputzu in Sardinia.

Heavy metal concentration in percolating porewater can thus be decreased considerably, even in the initial stage, when leachate from the waste contains, for instance concentrations of 700 mg/l of zinc, and more.

Similar tests for the immobilization of arsenate, showed that the transformed red mud granules were only about 5 times less efficient than the best commercially available adsorbent of granulated ferric hydroxide at €1500/ton.

Meaning that transformed red mud granules are cost efficient at €300/ton, while they are more crystalline and more stable, better binding the arsenate on the long term, and suited to be left in the natural environment.

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# €1500/T ELECTROKINESIS

In a third case we can see that the immobilization capacity of minerals improves if we can control protonic and electronic charge, as with electrokinesis.

One observes that in soil contaminated by negatively charged oxyanions, such as chromate (normalized initial chromium concentration C/C0, red dotted line), these will move towards the positively charged acid anode, and then adsorb prematurely on nearby positively charged, acidified soil (12-volt Chromium blank, yellow line).

This can be largely prevented, when placing alkaline transformed red mud near the anode. Then, the acid from the anode is neutralized, much less chromate adsorbs on the soil and more can be removed (12-volt Chromium with Transformed Red Mud, green line), bound tightly during adsorption on the acidified transformed red mud, and left in place.

Here it appears that the increased removal efficiency saves electricity costs of €1500/ton of used transformed red mud.

# INDUSTRIAL MINERALS

**Alkaline - acid mineral mix for heavy metal precipitation and arsenate adsorption**

Treated waste disposal site with internal permeable reactive barrier

External PRB decreases concentrations a 1000 times down to discharge limits

# ALKALINE / ACID MINERAL MIX, FOR HEAVY METAL AND ARSENATE

When we were ready to start our biggest project with Montana, a fourth case, the rehabilitation of the Baccu Locci lead arsenic mine site in Sardinia, the bauxite refinery was put on hold and our transformed red mud plant had to be closed.

In a very short time, GeoChemTec had to design alternative powders and granules, made from readily available industrial minerals, with similar properties.

That meant, enough alkalinity to allow for the immobilization of heavy metal cations, and with the extra surface area needed for the adsorption of arsenate oxyanion, mobilized by the increase in hydroxyl ion concentration.

# INDUSTRIAL MINERALS

Alkaline - acid minerals for heavy metal precipitation and arsenate adsorption

**Treated waste disposal site with internal permeable reactive barrier**

External PRB decreases concentrations a 1000 times down to discharge limits

# TREATED WASTE DISPOSAL SITE WITH INTERNAL PRB

At Baccu Locci we constructed an internal permeable reactive barrier at the foot of the waste rock disposal site, surrounding a slotted pipe, for pre-treating the leachate, transported to a discharge pipe.

The new mineral mixture was added to truckloads of the solid waste rock. As it was rather potent, so that only kilos were needed per truckload, it had to be added manually. The composition and quantity were continuously re-calculated, following the results of leachate tests in a laboratory on site.

| | S/cm | | | ppb | | | |
|---|---|---|---|---|---|---|---|
| pH | EC | Al | As | Cd | Cu | Mn | Zn |
| 4.8 | 8.2 | 33400 | <1 | 9630 | 15420 | 34930 | 394200 |
| 9.1 | 7.3 | <1 | <1 | 24 | 7 | 32 | 106 |

# INDUSTRIAL MINERALS

Alkaline - acid minerals for heavy metal precipitation and arsenate adsorption

Treated waste disposal site with internal permeable reactive barrier

**External PRB decreases concentrations > 1000 times down to discharge limits**

# EXTERNAL PRB DECREASE > 1000 TIMES TO DISCHARGE LIMITS

Very high concentrations occur in the acid rock drainage leaving the disposal site by the discharge pipe and they must be decreased down to strict surface water discharge limits.

The strong relief and the limited space ask for a small and very efficient external reactive barrier to immobilize the heavy metals.

Therefore, two filters are filled once a year with porous mineral granules of variable strength and down current increasing capacity.

The water flows only at a few cubic meters per day, and then alternatingly under and over the septa between the compartments in the filter.

After the first filter is exhausted, due to precipitation of aluminum gel, decreasing the residence and reaction time, one switches to the second filter.

The high efficiency of the filters follows from the values showing the good removal of cadmium and the strong decrease of concentrations, for instance of zinc, from almost 400 mg/L down to 0.1 mg/L in the discharged water.

The spent filter material is classified as inert, according to prescribed 24 hours distilled water leaching tests, and is disposed-off in a non-hazardous waste site.

# WHAT IS NEXT

**Improved deep bed filter for treatment of acid mine drainage**

Spent filter material for mining waste rock treatment

Geochemical technology unleashed into environment

# IMPROVED DEEP BED FILTER FOR ACID MINE DRAINAGE

A mineral filter is also used for treating acid mine drainage, coming from the San Riccardo mining gallery, again at Baccu Locci.

Thanks to the relatively low concentrations of heavy metals, in the order of few tens of milligrams per liter, we can get concentrations below discharge limits, despite much higher flow rates of tens of cubic meters per day.

Only, during several days following winter rainstorms, the filter fails temporarily, when influent concentrations can rise a factor ten.

So, next year Montana and GeoChemTec are going to improve the efficiency of the filter, with a better distribution of porous mineral granules of different reactivities.

We also might like to use locally available mineral products now, to decrease transport costs of the filter materials.

And we like to prepare readily accessible treatment protocols, so that the filters can be well managed, also by local non-specialized operators.

# WHAT IS NEXT

Improved deep bed filter for treatment of acid mine drainage

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# SPENT FILTER MATERIAL FOR MINING WASTE ROCK TREATMENT

The spent filter material, that can no longer maintain strict discharge limits at relatively high flow rates, is not yet exhausted. It is still very effective at lower percolation rates and longer reaction times, as for instance during percolation through soil or mining waste rock.

Therefore, instead of disposing the granules in dedicated sites for non-hazardous waste, we should also try to re-use them for treating acid rock drainage, and help producing fertile soil, when mixing with mining waste rock.

There are already some promising results of testing this concept, using mine drainage from gallery Fais of the Montevecchio mine in Sardinia, flowing at up to 50 L/s with 1000 mg/L of zinc.

# WHAT IS NEXT

Improved deep bed filter for treatment of acid mine drainage

Spent filter material for mining waste rock treatment

**Geochemical technology unleashed into open environment**

# GEOCHEMICAL TECHNOLOGY UNLEACHED INTO NATURE

In conclusion, we presume that geochemical technology with reactive minerals, will play an important role in better management of abandoned mining waste in the natural environment.

Where disposal sites for mining waste rock are constructed onsite and mining wastewater is treated passively in new types of mineral filter.

Not aiming at complete isolation of heavy metals, but allowing for controlled leaching, not resisting, but going along with the geochemical cycle.

We can observe that long abandoned historic mining waste sites have already largely adapted to climate, relief, and the dynamics of the geochemical cycle.

The most instable, readily erodible, and leachable parts are already gone, as demonstrated by the example of a strongly eroded, over-filled tailing pond of the historic lead-silver mine of Balya in Turkey.

From a geochemical technology point of view, it is suggested to not dig up this waste, reactivate it, and then dispose the problem elsewhere.

Better to use geochemical technology on site, for instance by covering it with a well-drained layer and a soil made from mining waste, mixed with reactive minerals.

# THANK YOU

## And go well with your geochemical cycle

Alberto Angeloni | Montana & Hans Zijlstra | GeoChemTec

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