TREATMENT OF ACIDIC MINE DRAINAGE AT LIBIOLA MINE, LIGURIA, ITALY

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Abstract
A series of field trials have been conducted using dealginated seaweed to absorb metals from acidic, iron-rich mine waters from the Libiola mine in northern Italy. A specific plant has been designed to treat these waters. These acidic waters have high Fe (230 mg/L), Cu (50 mg/L) and Zn (8.7 mg/L) concentrations, and needed a buffering treatment prior to reaction with the dealginated seaweed. NaOH, Na_2CO_3 and slurry from fine-grained dealginated seaweed were tested as buffering agents in the field tests. The NaOH treatment removes Fe and also other metals (Cu, Zn, Ni, Mn) by up to 90% of the inflow concentration, then the seaweed further removes 60% of Cu and Mn, as well as some Zn. Similar results were obtained from the Na_2CO_3 treatment, although the removal of metals from solution is more efficient (50% Cu, 80% Ni, 90% Mn and Zn). Although limited in duration, the results confirm the effectiveness of the dealginated seaweed as a metal absorber in the treatment of acid mine waters as well as circum-neutral mine drainage.

Introduction
Sulfide waste disposal is an important environmental issue both in extensively mineralized areas and from point sources. Crushing, grinding, washing, smelting and other operations to extract and concentrate metals increase the mobility of chemical elements in the surrounding environment through normal biogeochemical pathways (Davies, 1980, 1983). The wastes from former mining activity still have high metal concentrations and may therefore represent a source of metal pollution for a long time after extraction (Davies, 1983). Severe environmental problems arise if pyrite is present in the mineralization leading to Fe- and metal- rich acidic waters (Nordstrom and Alpers, 1999), a feature that is common in the study site, the pyrite-chalcopyrite mine of Libiola, in northern Italy.

The study area is located near the village of Libiola (Genoa province), about 10 km NE from the town of Sestri Levante (Fig. 1). The mineralization is hosted in pillow and brecciated basalts (Ferrario and Garuti, 1980) and the mine was already known in the Copper Age (about 2500 B.C.; Campana et al., 1996), but economic exploitation started in the 17th century and ended in 1962. Mining was conducted by both open pit and underground operations. Nowadays several open galleries and waste dumps testify the past mining activities. The physico-chemical characteristics of water discharges have been described in several recent papers (Dinelli et al., 1999, 2001; Cortecci et al., 2001; Dinelli and Tateo, 2002; Marini et al., 2003; Accornero et al., 2005) and all indicate the presence of acid mine drainage, characterized by high metal loadings, dominated by Fe, Al and Cu.

Three sites (Ida, Castagna, Margherita) have almost constant discharge during the years affecting the quality of surface drainage in the area (Dinelli et al., 2001; Accornero et al., 2005). Of these, the Margherita discharges displays rather constant composition over time and has a pH generally ranging between 6 and 7 (Cortecci et al., 2001; Dinelli et al., 2001; Dinelli and Tateo, 2002; Accornero et al., 2005). The other two sites were chosen for the monitoring program: the Castagna adit (Fig. 1) is at the lowest altitude, with constant flow and with limited precipitation of solid ochreous phases (if any schwertmannite); the Ida adit (Fig. 1) has continuous discharge and is characterized by intense precipitation of ochreous phases (mostly schwertmannite and goethite). This latter was the site chosen as the field test site in November 2006.

The results of a three year monitoring program on these acid water sources are summarized in Table 1. A large variation range is observed for all the chemical parameters, with maximum concentrations generally observed in the dry summer period and more diluted concentrations typical of rainy autumn. The field trial has been conducted during a relatively high-flow period in November 2006.

The monitoring of waters, the characterization of solid secondary products in the Libiola area and the field test trial for the dealginated seaweeds were conducted in the framework of the 2003–2006 EU-LIFE Environment Project "BIOMAN" (BIOadsorption of Metals from Abandoned mines) that aimed at the development of an innovative method for the remediation of mine drainage waters. This site was chosen as a test for mine waters in different environmental and climatic conditions compared to Welsh mines, but is also characterized by the problem of high Fe concentrations which must be dealt with before treatment with dealginated seaweed. In similar cases typical mine water treatment options such as neutralization and precipitation of Fe-oxyhydroxides (e.g. Jambor et al., 2003) represented the preferred treatment options and such treatments were also considered in the setting up of the field trial in Italy.

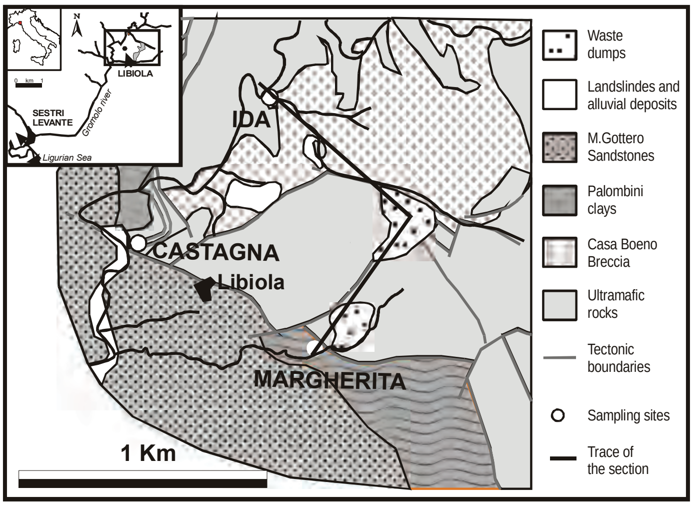

Figure 1. Geological sketch map of the Libiola mine area and indication of the monitored sites.

Table 1. Range of data of the 3 year(2003-2006) monitoring program of the Libiola mine water.

	Castagna	site A	Ida	Site B	Margherita	Site C
	min	max	min	max	min	max
T (°C)	10.2	17.6	10.2	17.2	12.6	18.2
pH	2.3	3	2.4	2.8	6.5	7.6
Eh (mV)	470	650	480	630	62	275
Cond. (µS/cm)	4500	14080	4060	7250	1700	2490
Cl (mg/L)	4	20	5.5	17	9.1	17
SO_4 (mg/L)	3850	9700	3150	5500	1290	1650
Alk. (mg/L HCO_3)	nd	nd	nd	nd	33.6	107
Na (mg/L)	12.5	58	9	42	7.1	18
Mg (mg/L)	368	1200	298	680	100	251
Ca (mg/L)	149	450	228	640	146	302.4
K (mg/L)	0.1	2	0.19	2.3	1	3.9
Al (mg/L)	59.5	270	40	120	nd	0.25
Fe (mg/L)	230	1010	210	421	0.059	0.4
Cu (mg/L)	45	250	46.2	99	0.1	6.6
Zn (mg/L)	20	60	20	45	2.3	6.6
Ni (mg/L)	3.7	8.8	1.8	3.7	0.12	0.7
Cr (mg/L)	0.8	2.54	0.2	0.6	nd	nd
Mn (mg/L)	6	10.5	2.9	6	0.1	1.2
	45 observations		45 observations		16 observations	

nd = not determined

Methods

Pilot treatment plants were designed to allow a contact time of about 15 minutes between the mine water and a bed of dealginated seaweed, based on the results of laboratory adsorption experiments (Perkins et al., 2007). Two sources of dealginated seaweed were available from manufacturers in Scotland (processing *Ascophyllum sp.*) and Denmark (processing *Laminaria sp.*), and these required pretreatment before they were suitable for use in the treatment plants (Hartley et al., 2007). For the Libiola test it has been necessary to add three more treatment stages before the final processing with dealginated seaweed in order to allow iron separation from the acid drainage and present water with proper quality for the dealginated adsorption (Fig. 2). The system was designed to treat a flow of 1 L/min. In the first stage of treatment a buffering agent was added to the mine water, different buffering agents were tested: 1M NaOH, 1M Na_2CO_3 and 1/6 by weight of a slurry made of fine-grained

dealginated seaweed. In the second treatment stage a flocculating agent was mixed with the mine water in order to speed-up the separation of solid particles. A third treatment stage uses a large tank to allow solid separation and "clean" water to flow to the dealginated seaweed treatment tank for complete cleaning.
The experiment with NaOH was conducted overnight, the Na_2CO_3 experiment ran for 4 hours whereas the slurry test started but could not be completed, however the efficiency and buffering capacity of this solution has been previously tested in the laboratory in order to evaluate the optimum operating conditions.
Temperature, pH, Eh and electrical conductivity were measured directly in the field, dissolved metal concentrations (Fe, Cu, Zn, Mn, Ni) were determined in filtered (0.45 μm) and acidified water samples by flame atomic absorption spectrometry (FAAS).

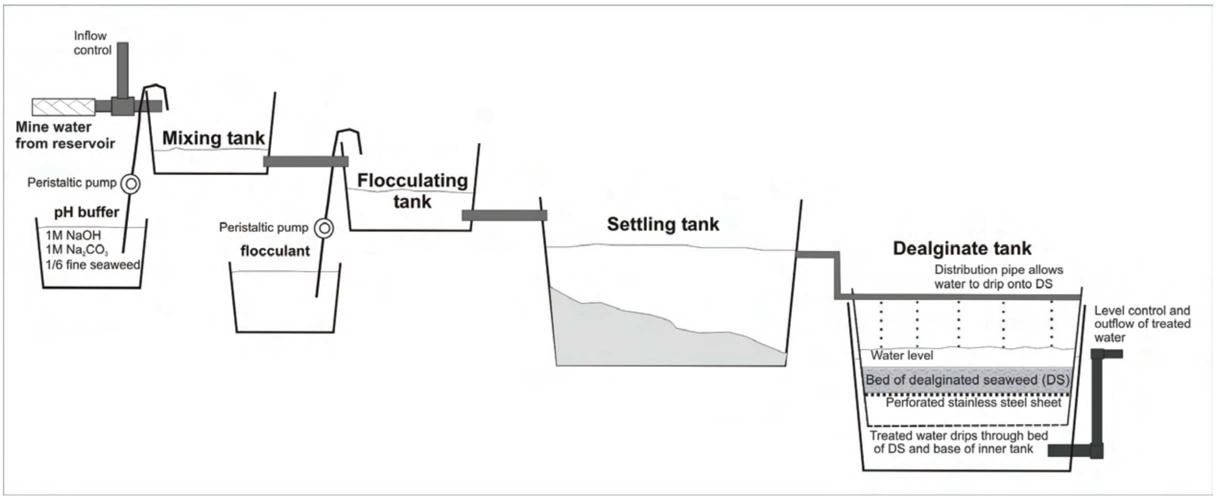

Figure 2. Scheme of the pilot treatment plant in Libiola, which included three separate treatment tanks to remove iron from solution.

Results and Discussion

Figure 3 shows the results of the field trials conducted in the Libiola mine area. These results indicate that the addition of NaOH and Na_2CO_3 raised the pH and contributed to the reduction of Fe concentration in solution. The flocculation stage also reduced all the other metals whereas the dealginated residue significantly separated Zn and Ni and reduced the concentrations of Mn and Cu. Its efficiency seemed to increase with time, however it was not possible to have a longer record due to a failure in the buffer pump that caused acidic water to flow directly into the dealginated seaweed. Nevertheless the dealginated seaweed did not lose its adsorption capacity but significantly reduced the Fe concentration, removed half of Mn and minor amounts of Zn and Ni (Fig. 4) as predicted in Fe-rich waters (Pearce et al., 2007). On the other hand copper was released to solution possibly indicating an exchange reaction with iron in the adsorption sites of the dealginated seaweeds.

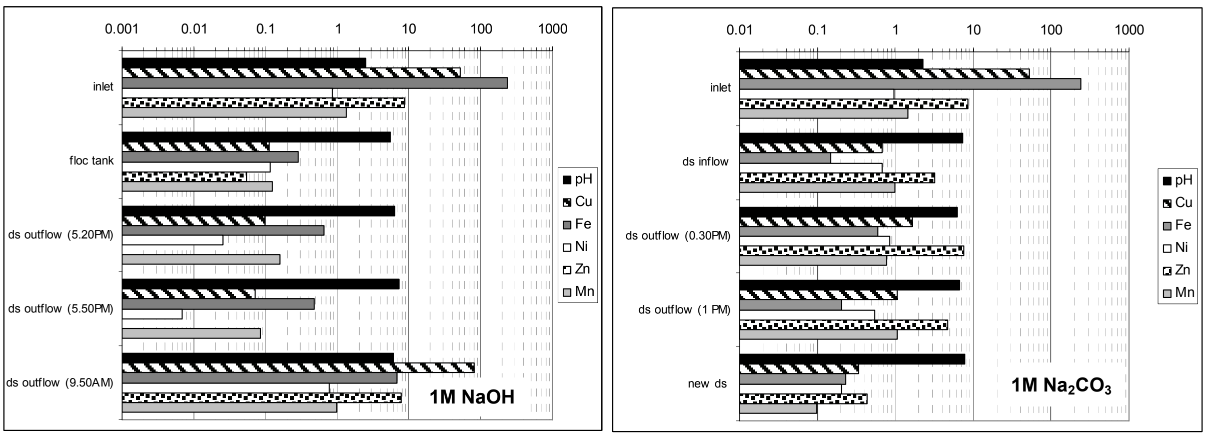

Figure 3. Changes in pH and concentrations of Cu, Fe, Ni, Zn and Mn (all concentrations in mg/L) using NaOH and Na_2CO_3 as buffering agents. ds (dealginated seaweed tank).

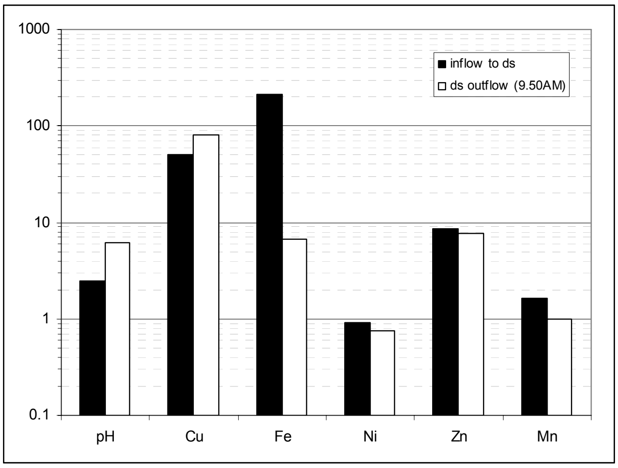

Figure 4. Changes in pH and concentrations of Cu, Fe, Ni, Zn and Mn (all concentrations in mg/L) between inflow and outflow in the dealginated seaweed tank after overnight flowing.

The Na_2CO_3 treatment led to a solution with slightly lower metal concentrations compared to NaOH, with the exception of Zn, which has been verified to have limited adsorption into the dealginated residue (Pearce et al., 2007). Also in this case the efficiency seems to vary with time, however with limited changes. The dealginated seaweed in the final treatment system was changed after the exposure to the Fe-rich waters. After the adsorbing material was changed the results obtained are significantly different (Fig. 3) showing the lowest concentrations in the outflow observed during the field trial.

Conclusions

Dealginated seaweed has proven to be an effective absorber of metals from mine waters with low Fe concentrations (<<0.1 mg/L) (Hartley et al., 2007; Pearce et al., 2007; Perkins et al., 2007) but waters with higher Fe concentrations pose some key issues to the active adsorbing life of the system. The field trials on the Fe-rich waters (230 mg/L) indicated some interesting results, although the system could not work for long time. The iron removal techniques proved to be very effective and the dealginated seaweed further improved the water quality.

Acknowledgements

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