DEALGINATED SEAWEED FOR THE BIOREMEDIATION OF MINE WATERS IN MID-WALES: RESULTS OF FIELD TRIALS FROM THE "BIOMAN" EU LIFE ENVIRONMENT PROJECT

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Abstract
A series of small scale field trials have been conducted using dealginated seaweed to absorb metals from circum-neutral mine waters in mid Wales. These waters, issuing from disused 19th century mines are often rich in Zn (up to 42 mg/L), Pb (up to 2.8 mg/L) and Cd (up to 100 μg/L) but are low in Fe (<<1 mg/L), a result of the dominantly sphalerite/galena mineralisation with very little associated pyrite. Pilot plants treating 1, 2 and 10 L/min show that in excess of 95% of the dissolved metals are removed from these mine waters for a period of time which depends on the volume of dealginated seaweed in the plant and the inflow concentration. Zinc is the first metal to become saturated in the dealginated seaweed, followed closely by Cd. In contrast, in some trials Pb removal continues at between 85-98% efficiency long after the dealginated seaweed had become saturated in Zn and Cd. Different sources of dealginated seaweed, which process different raw materials (*Laminaria sp* or *Ascophyllum sp*), behave in a different manner, with the processed *Ascophyllum sp* absorbing most metal.

Introduction
Mid-Wales has a long history of metal mining dating back to the Bronze age, but the majority of mining was undertaken in the late 18th and 19th centuries. This has left a legacy of old mine workings and spoil tips which liberate high quantities of dissolved metals into the aquatic environment (Fuge et al., 1993a, b; Fuge et al., 2000; National Rivers Authority, 1994).
In mid-Wales, the mineralisation is dominantly galena-sphalerite vein type, containing sparse chalcopyrite, but is typically pyrite/marcasite free. This generates mine drainage waters which have high Zn, Pb and Cd, but are circum-neutral and Fe poor (see Table 1), although 2 mines (Cwm Rheidol and Cwm Ystwyth) are pyritic and produce Fe-rich waters. The area around Aberystwyth, mid-Wales, contains 38 of the 50 worst polluting metal mines in Wales (Environment Agency, 2002), many of which were monitored during the present study (see Fig. 1).
The low-Fe content and near neutral character of the mine waters in the mid Wales area does not lend itself to the more traditional mine water treatment options such as neutralization and precipitation of Fe-oxyhydroxides (e.g. Jambor et al., 2003) and thus a novel approach is required to remediate these waters.
Dealginated seaweed has the ability to absorb high concentrations of metals from water, and this aspect of its character has been exploited as part of the "BIOMAN" project funded by the EU Life Environment programme to demonstrate its use in mine water remediation. A series of laboratory scale experiments (Perkins et al., 2007) defined the adsorption characteristics of the dealginated seaweed, and these aspects (capacity, rate of reaction) were used in the design of a series of pilot treatments plants to be used for field testing in Wales and in also in Italy (Dinelli et al., 2007).

Table 1. Range and typical metal concentrations in Fe-poor waters draining metal mines sampled in mid-Wales (see also Fig. 1). Concentrations in μg/L.

	Minimum	Maximum	Typical
pH	4.8	7.9	6.5
Fe	<10	500	<100
Zn	<5	42000	600-1000
Cd	<0.1	99	~1-5
Pb	<5	1350	150-300

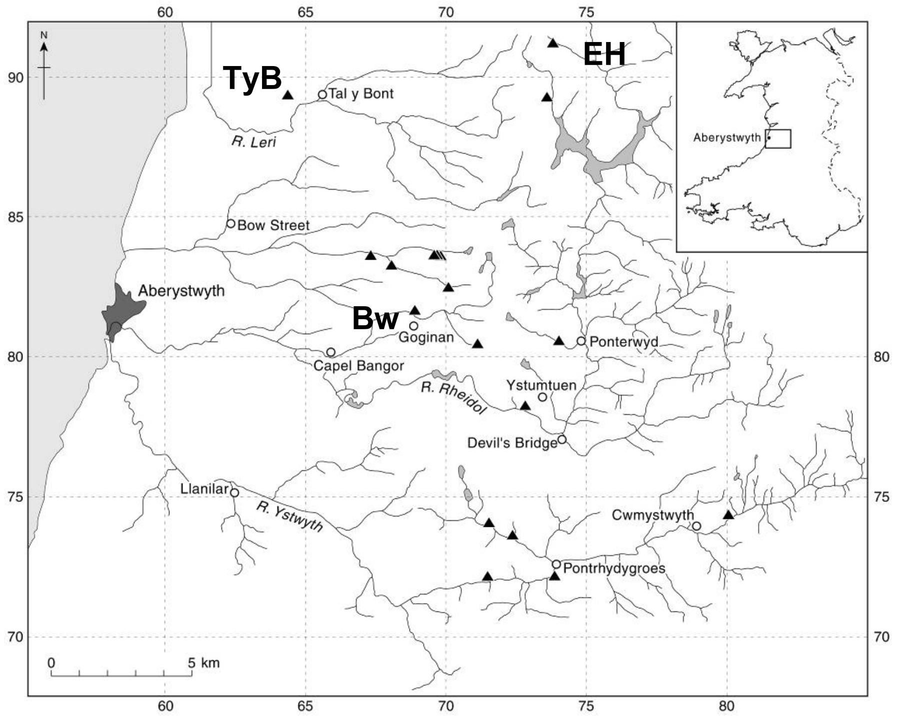

Figure 1. Metal mines in the mid –Wales area sampled on a monthly basis during this study. Locations of treatment plant trials are indicated: EH – Esgair Hir, Bw – Bwlch, TyB – Tal-y-Bont.

Methods

Pilot treatment plants were designed to allow a contact time of about 15 minutes between 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). A cartoon of the design of the 1 L/min treatment plant and a photograph of the 2 L/min "tandem" treatment plant is shown in Figure 2. The "tandem" treatment plant, essentially 2 side-by-side 1 L/min plants was designed to allow the comparative testing of the different sources of dealginated seaweed.

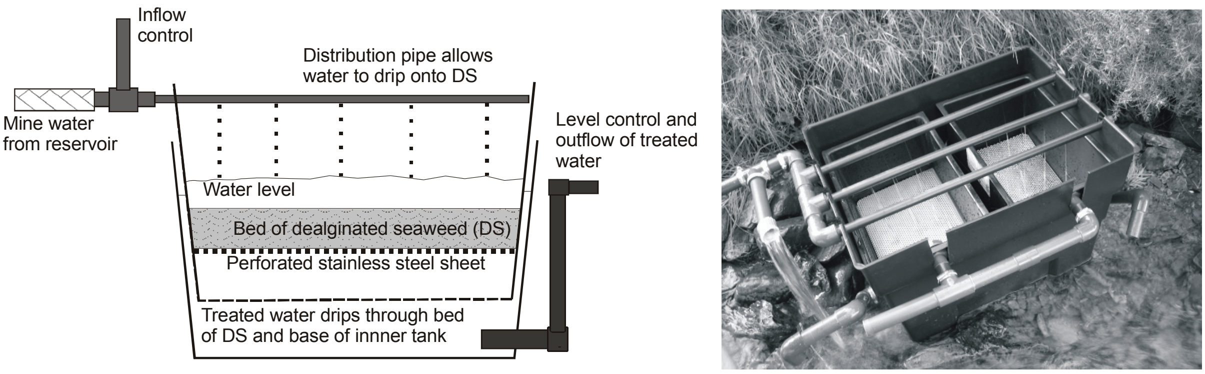

Figure 2. Left: Cartoon of the design of the pilot treatment plants. Right: Photograph of the tandem 2 x 1 L/min treatment plant, showing the flow control (at left) the distribution pipes across the top, and the outflow pipe to the right.

Results and Discussion

Figure 3 shows the amount of metal removed by a treatment plant at the Bwlch mine, mid Wales. Here the "tandem" 2 x 1 L/min plant was used, with the inflow waters containing on average 20 mg/L Zn, 60 µg/L Cd and 900 µg/L Pb, at a pH of ~6. In this trial, material from both Scotland and Denmark was tested in side-by-side 1 L/min systems, each containing 2 kg of dealginated seaweed in a bed about 10 cm thick. For both materials, within 30 minutes of operation, in excess of 90% of Pb, Zn and Cd were removed from solution. Zinc removal by the Scottish dealginated seaweed starts to decrease from a maximum of about 97% after 12 hours until, at about 5 days the system starts to release Zn back to the water, as result of continuing ion exchange processes. Cadmium removal starts to decreases at about 36 hours, and starts being released at the same time as Zn. In contrast, in excess of 95% of the Pb is removed for the entire 4 week duration of the experiment. Analysis of the bed of dealginated seaweed shows that Zn was evenly distributed throughout the bed (at a concentration of about 1.3 wt % dry weight), but that all the Pb was retained in the top 15 mm of the layer, reaching a concentration of about 3.2 wt %. This process probably relates to different uptake sites in the dealginated seaweed showing a preference for particular metals, and Pb removal could thus be expected to continue for up to ~6 months in this trial. While the overall pattern of uptake displayed by the Danish material is similar to the Scottish dealginated seaweed, the uptake efficiency starts to decreases almost immediately, becoming saturated for Zn and Cd at about the same time. The Danish material however has an overall capacity of about 50% that of the Scottish material for Zn and Cd. Like the Scottish material, the Danish dealginated seaweed, continues to remove Pb for the duration of the experiment, but less efficiently (at about 90% instead of >95%). These differences reflect the different uptakes by the raw species processed.

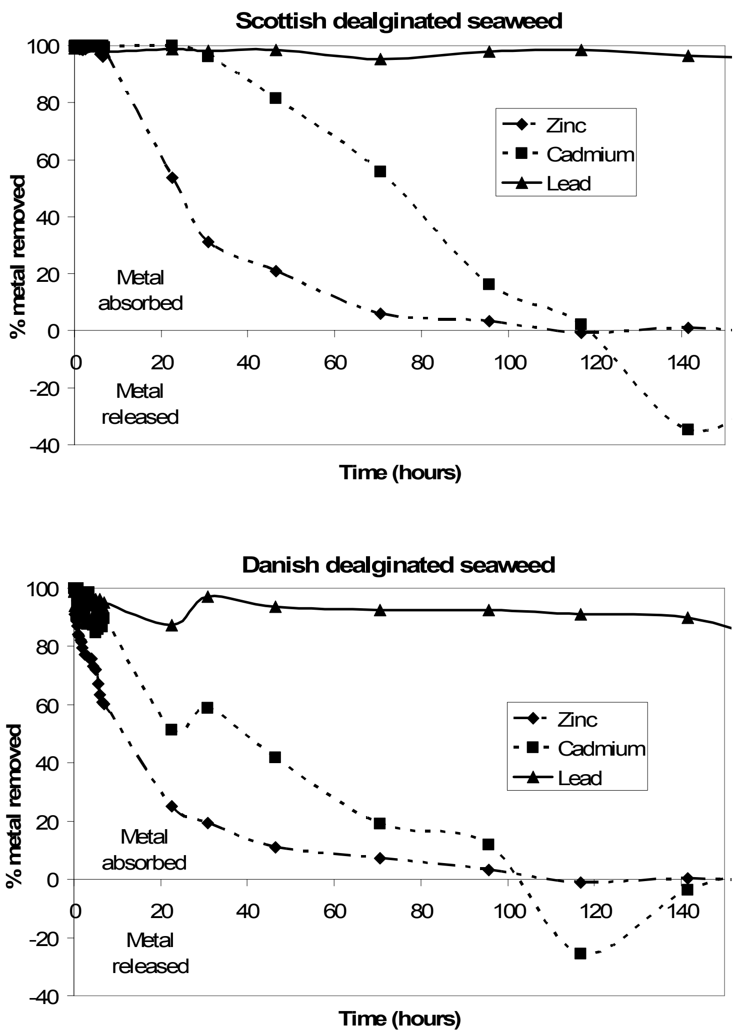

Figure 3. Percentage metal removal for the 2 x 1 L/min "tandem" treatment plant at Bwlch mine, comparing the performance of the two sources of dealginated seaweed.

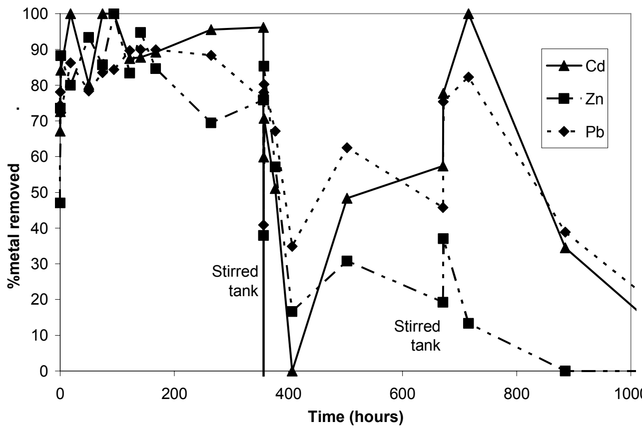

Figure 4. Percentage metal removal for the 1 L/min treatment plant at Esgair Hir mine using Danish dealginated seaweed. The bed of dealginated seaweed was stirred at ~360 hours and at ~670 hours.

Water draining from an adit at the Esgair Hir mine has a pH of about 6 and contains a trace of Fe, occasionally reaching about 0.4 mg/L, but typically at <0.1 mg/L, most probably the result of the dissolution of an Fe-carbonate gangue mineral. This gives a slightly ochreous drainage. This water contains about 370 µg/L Zn, 170 µg/L Pb and 1.5 µg/L Cd, approximately 2% of the Zn content and about 20% of the Pb of the Bwlch mine drainage. A plant containing the Danish dealginated seaweed and treating 1L/min was deployed at Esgair Hir for 66 days, and monitored regularly (see Fig. 4). The metal removal as a percentage was comparable to that at Bwlch, but because of lower concentrations remained high for far longer. By 15 days (360 hours) a fine precipitate of ochre had formed on the surface of the bed of dealginated seaweed which reduced the flow of water through the bed. The bed was stirred to renew the flow at this time, and this process was repeated at about 680 hours (28 days). This caused some disturbance to the adsorption efficiency, but from the data in Figure 4 a general trend of high adsorption for the first 15 days, slowly dropping thereafter can be observed until Zn release starts at around 37 days (900 hours). Interestingly Pb adsorption falls off here at about the same time as Cd, being released at 50 days, although flows by this point were almost nonexistent.

Conclusions

Dealginated seaweed is an effective absorber of metals from mine water, removing up to about 4% of its own weight of Pb, Zn and Cd. For mine waters which are low-Fe (<<0.1 mg/L) it offers an effective means for remediation, and depending on the concentration of the inflow waters, modest sized treatment plants could be designed to have a lifespan of several months before any maintenance is required. Small amounts of dissolved Fe cause the bed of dealginated seaweed to clog with precipitated ochre and neutralization/metal removal needs to be considered if Fe-rich waters are to be treated. The different sources of dealginated seaweed absorb different quantities of metals, with the Scottish material, derived from *Ascophyllum sp.* having about twice the metal capacity of the Danish material from *Laminaria sp.*, a reflection of metal uptake behaviour in the live seaweeds.

Acknowledgements

We are grateful to the European Union Life Environment programme for financing this demonstration project (EU Life Environment Project LIFE03ENV/UK/000605). We would also like to thank Mr Hughes of Trawsnant Farm, Cwmmerfyn, for his interest in the project and allowing us such ready access to the drainage from the Bwlch mine, and to the Forestry Commission for access to the Esgair Hir mine site.

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