BAUXSOL™ TECHNOLOGY TO TREAT ACID AND METALS; APPLICATIONS IN THE COAL INDUSTRY[1]

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Abstract. The mining of coal most often leads to the development of Acid Rock Drainage (ARD) because during peat accumulation anoxic and reducing conditions establish and an availability of sulphate and reducible iron, even at low concentration, leads to the formation of iron sulphides (mostly pyrite). Once exposed oxidation and acid generation occurs, which may mobilize trace metals from the coals. The combination of acid and metals can seep into water ways where it can effectively sterilize many km of stream, and deposit substantial quantities of iron oxy-hydroxides. Frequently waste rock and coal washery tailings are stored where they provide suitable habitat for bacteria that accelerate the oxidation of pyrite and the production of acid.

Aberdare East colliery is a former underground mine located in Cessnock, New South Wales, Australia. Coal washery tailings from the mine are impounded in a series of overlapping stacked cells in a small catchment. Relatively clean water enters the south eastern extent of the tailings and moves to the northwest down the hydrological gradient, and exit the north western batter slope into the a small creek. During flow through the tailings salinity, metal content, redox potential, and temperature all increase; solution pH decreases. Investigations indicate that the impoundment contains 109,445 m^3 of water, 337,793 m^3 saturated fines, 720,113 m^3 of unsaturated fines, and 184,568 m^3 of clay capping.

Treatment rates indicate that the water requires 5.123kg/m^3 of Bauxsol™ Acid B Extra™ C5T5 blend (561 t) and that a further 24,000 t of Bauxsol™ ViroMine™ is required to prevent further acidity at the site being generated. This compares favourably with lime of 0.951 kg/m^3 for the water (104 t) and 32,750 t to prevent further acid production from the tailings. Additional benefits from the Bauxsol™ based treatments are lowered sludge volumes during water treatment, increased chemical stability of the residues and therefore greatly reduced disposal costs, a decreased susceptibility to dissolution of the ANC from the soil/tailings profile that reduces the possibility of having to reapply after 5 or 10 years and, consequently, a reduced safety margin for the Bauxsol™ application is required.

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Introduction

The Bauxsol™ technology involves a diversity of procedures and products that can be used in environmental remediation and management programs but fundamentally, the technology involves the use of a complex cocktail of minerals prepared by chemical and physical modification of the caustic red mud residues generated during alumina production by the Bayer process (McConchie *et al.*, 1996, 1999). The useful properties of this cocktail of minerals were first recognized in 1992 and following detailed laboratory investigations, a joint venture with Virotec International Ltd. was developed to carry out full scale field trials and to commercialize the technology. A successful pilot scale trial (1.6 ML) was completed in early 2000 (McConchie *et al.*, 2000b) and full scale treatment of a commercial 1,500 ML tailings dam was completed a few months later; large scale treatment and revegetation of sulphidic mine tailings and waste rock was also successfully completed in 2000.

The original mixture of very fine grained minerals that forms the basis of the Bauxsol™ technology usually includes: abundant hematite, boehmite, gibbsite, sodalite, quartz and cancrinite, minor aragonite, brucite, calcite, diaspore, ferrihydrite, gypsum, hydrocalumite, hydrotalcite, lepidocrocite, p-aluminohydrocalcite, portlandite and whewellite, titanium oxides, and a few low solubility trace minerals (McConchie *et al.*, 1999, 2000b). The exact composition depends on the composition of the bauxite used at each refinery, operational procedures at the refinery, how the caustic red mud is neutralized and what product blends are chosen. Patented product blends can be prepared by adding small quantities of natural minerals or other chemical substances to the original mineral suite to improve its performance for particular treatments. Irrespective of its exact composition, the initial mineral mixture has a high acid neutralising capacity (up to 7.5 moles of acid / kg depending mainly on operational procedures at the refinery) and a very high trace metal trapping capacity (usually greater than 1,000 milliequivalents of metal / kg); it also has a high capacity to trap and bind phosphate and some other chemical species and is an excellent flocculant.

The mixture of minerals has a plastic limit at about 33% moisture, a liquid limit at about 53% moisture and a linear drying shrinkage of 7.5%. Although the mineral particles are very fine grained (about 80% have a particle size of less than 10 microns), the material is non-dispersive and its addition to some sulphidic soil, sediment, or dredge spoil can increase strength as well as eliminate the potential generation of acid and release metal.

Bauxsol™ reagents can be produced to suit individual applications (e.g. slurries, powders, pellets and porous blocks) and the products have a near-neutral soil reaction pH (typically

between 8.2 and 8.6) despite its high acid neutralising capacity. This soil reaction pH is close to neutral and the Toxicity Characteristic Leaching Procedure (TCLP) results (See Table 7) are sufficiently low that it can easily be transported and it is safe for unskilled workers to handle. The residual material can often be recovered and reused in other applications (e.g. material used to remove phosphate from sewage effluent can later be used to stabilize sulphidic waste rock or tailings).

Metals bound when Bauxsol™ technology is used to treat contaminated water are held very tightly and only a small proportion can be released even when the solid residue is leached at a pH of 2.88; furthermore, the longer the residue is left to age, the more tightly the metals are held. It has also been found that ageing residue develops new metal trapping capacity such that if the residue is left in a tailings dam or pit lake after initial treatment has been completed, the metal concentrations in the water will continue to decrease for at least twelve months (Clark *et al*, 2000).

This paper explores the possible applications of Bauxsol technology in the coal mining industry using data from the Aberdare East mine, Cessnock, Australia as an example.

Abadare East Mine Site

The Aberdare East study site is located in close proximity to Cessnock, in the Hunter Valley, approximately 120 kilometres north of Sydney, 40 kilometres west of Newcastle and 30 kilometres from the coast (Fig. 1).

The washery wastes are adjacent to the main shaft (now sealed), a derelict coal laboratory and an area used for the underground pit top buildings including a coal processing plant. The washery waste area is set within a site that contains rehabilitated coal product and reject dumps, old quarries a hall road network, treatment areas and natural bushland (Water Resources Consulting Services 1999).

The washery waste can be divided into several different levels according to its topography (Fig. 2). Level A is the lowest area (~80m ASL) on the site and is the area that most of the water seeps. Level B is the level immediately south east of Level A (~86m ASL). Level C is the highest level (~90m ASL) south east of Level B. Level D is slightly lower in elevation than Level C (~87.5 ASL) ad Level E slightly lower again (~85.5m ASL). Level F represents the drainage system around the site, the majority of water being held in the eastern corner. Level G is similar to that of Level B.
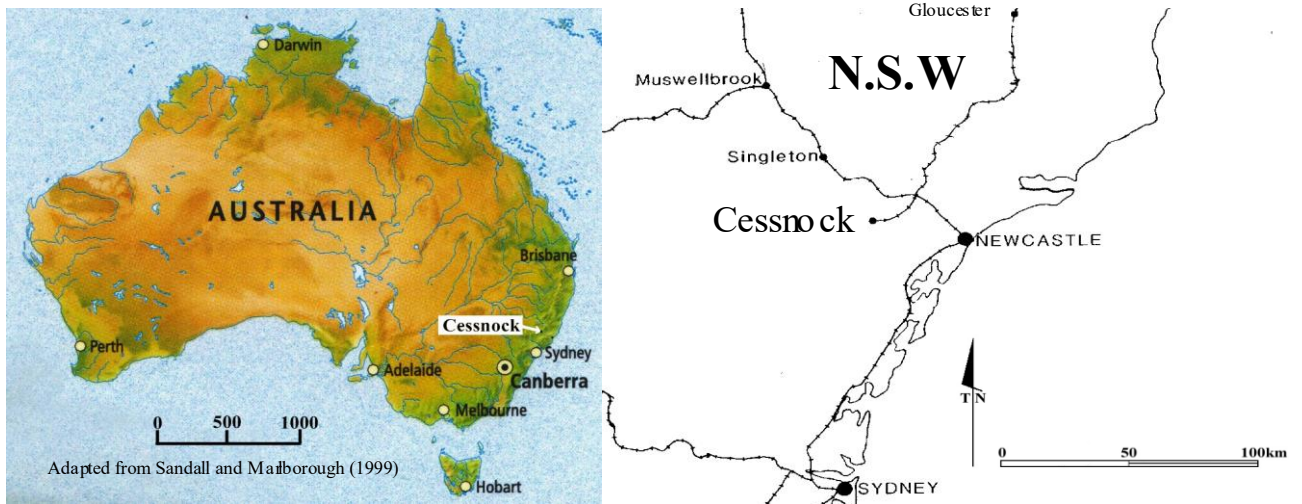
Figure 1. The location of Cessnock, NSW Australia.

Figure 2. The location of the study site in Cessnock, NSW, Australia, areas A, B, C, D, E, F, and G are different topographic levels of the washery waste.

Aberdare East Sampling

Nineteen test pits were dug into the coal tailings, 18 into the slimes and 1 into a dam wall (Fig. 3), using a long reach excavator. Thirteen piezometers were emplaced into these pits, and an additional 3 piezometers placed into areas where the excavator could not move to (mostly on area A; Fig, 2). Coal samples from the sampling pits were analysed for their pyrite contents, by the chromium reducible sulphur method (Sullivan et al, 1998), EC, reaction pH, soluble acidity (Lin et al, 2000) and visual grain size measurements taken. Water samples were taken from the seepages and analysed for pH, EC, and metals contents (Fe, Al, Cu, Cd, Pb, Zn, Cr, Ni, Co, Mn, As, & Ag). Water samples were then reacted with ViroMine™ blends, $Ca(OH)_2$, and MgO, until a neutralization pH of 8.3 was achieved. The remaining solids were then assessed for stability using the standard TCLP Leach system (USEPA, 1996).

The whole of the tailings was also surveyed using a standard dumpy level, some 3000 survey points and 65 bench marks, to provide a 3D model of the site. Water heights, thessian polygon overlays (for volume weighted averages), tailing thicknesses, cover thickness were modelled using Vulcan Forge™ software to estimate volumes of saturated and unsaturated tailings, ground water volumes, and cover volumes. These physical data combined with the geochemical data gathered gave an overall assessment of the quantities of Viromine™ and Lime required to achieve neutralization.

Results and Discussion

Treatment of Sulphidic Mine Tailings and Waste Rock

Sulphidic mine tailings and waste rock usually contain sulphide minerals (particularly pyrite) that can oxidize when exposed to atmospheric oxygen and moisture to release acid, metal ions and sulphate ions; the acid generated in the process can leach additional metals from any other rock material that comes in contact with it (Evangelou, 1995). Oxidation of the sulphides in these materials usually begins slowly, but once the pH of the pore water falls to about 3, ferric iron can catalyse the breakdown of sulphides and the process can accelerate rapidly. Oxidation of the sulphides can also be accelerated by approximately a million times by common sulphur and iron oxidising bacteria (Bigham *et al*., 1990; Evangelou, 1995). Antibiotics have been used at some mines to prevent microbially accelerated decomposition of

sulphides, but this can only ever be a short term strategy and there is a risk that antibiotic resistant strains of the bacteria will develop.
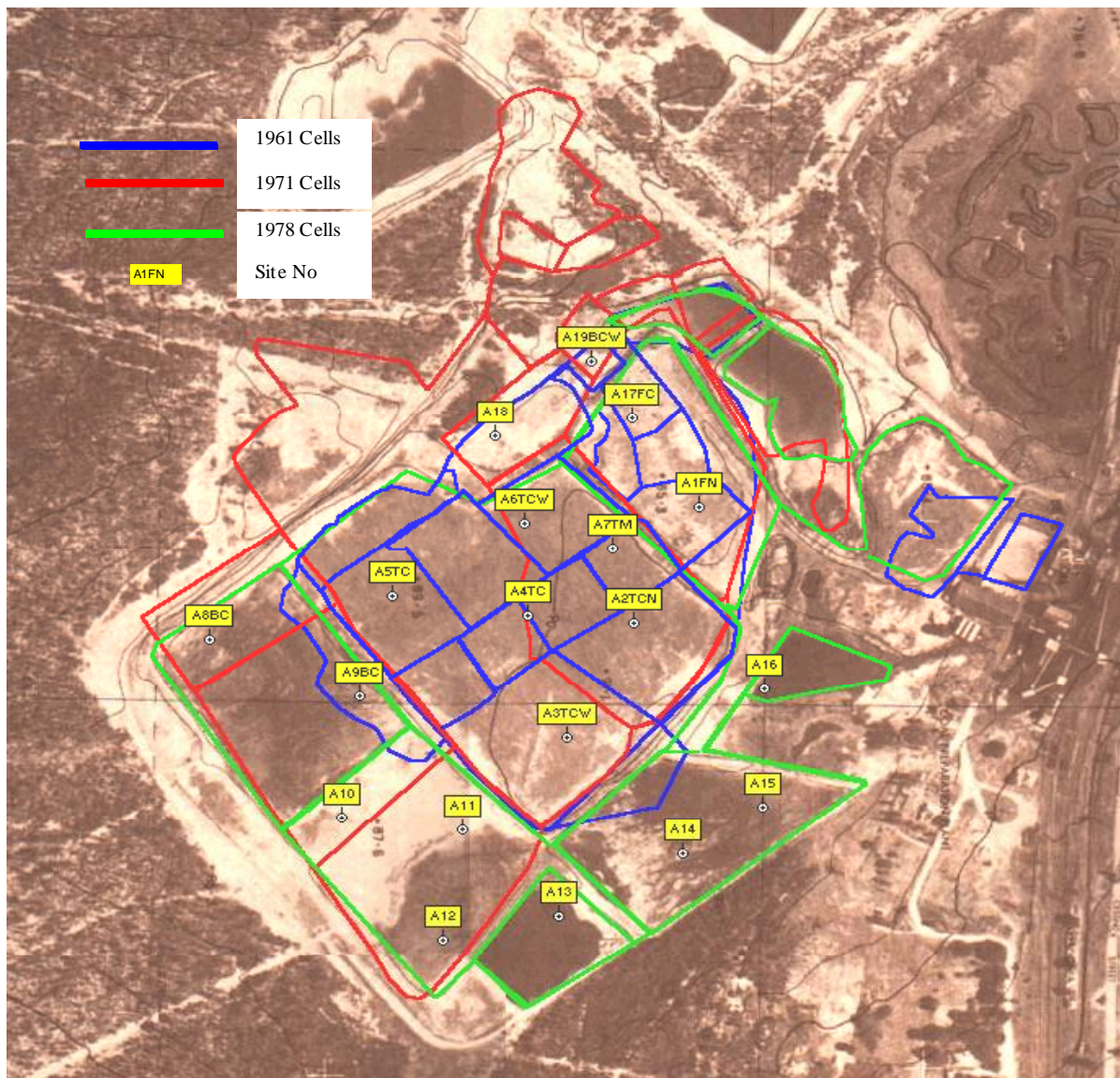
Figure 3. Cell structures within the Aberdare washery waste pile

The most widely used strategy to manage sulphidic mine tailings and waste rock is to isolate them from atmospheric oxygen and water by placing them in lined and capped impoundments. However, there are a number of major problems with using lined and capped impoundments (Fanning *et al*., 2001), which could well be described as a 'cover up' rather than a 'clean up' strategy, including:

1) no matter how well the impoundment is designed it can not provide a permanent solution because at some stage it will inevitably fail (no engineered structure will last forever),

2) confinement of large quantities of sulphidic material is not always practical,

3) although caps and linings can prevent the production of acid leachate by infiltrating rainwater, they seldom completely prevent the escape of leachates with groundwater, and

4) capped impoundments can only ever be revegetated with small plants because the roots of large trees can puncture previously impermeable caps. Therefore, a capped site will require perpetual O&M costs.

Where the escape of leachates from impoundments is anticipated, PRBs can be placed to treat the leachate (Titchenell & Skousen, 1996; Powell et at., 1998; Skousen et al., 1999) or the leachate can be diverted to a dam or chemical processing facility for treatment as described for AMD/ARD waters, but these approaches require ongoing expenditure and are not 'walk away' strategies.

Sulphidic mine tailings and sulphidic waste rock can also be managed by blending in acid neutralising chemicals such as lime, or by encapsulating the sulphides in unreactive materials such as silica or phosphates (Evangelou & Zhang, 1995, Evangelou 2000). Several effective encapsulation technologies have been developed, however they are expensive to apply. Blending the sulphidic wastes with appropriate quantities of lime is cheaper but the lime is slightly soluble and over time it can be leached from the wastes before all the acid that needs to be neutralized has been produced. Furthermore, the presence of lime can increase the availability of bicarbonate ions that can catalyse the decomposition of the sulphides and accelerate acid and trace metal release, particularly where insufficient lime was added originally or where some of the original lime has been leached out by water (Evangelou & Setra, 1997).

As with the use of lime in PRBs, the development of coatings on particles of lime mixed with the sulphidic wastes and the precipitation of gypsum can reduce the effectiveness of the treatment. Many organisations that have used lime to treat sulphidic tailings and waste rock have reported serious problems with meeting environmental quality targets, particularly a few years after the treatment was completed. Although the application of lime remains the most widely used management option, Ward *et al.*, 2000 and Lombi *et al*. 2001 reported several problems associated with its use, including:

1) because lime is slightly soluble in rainwater and most groundwaters, if a series of wet seasons precede a drought, much of the lime may have been leached from the soil before the acid that it was supposed to neutralize is produced,

2) for some ecosystems, adding too much lime may cause more environmental problems than it solves,

3) bicarbonate ions, which form when some lime dissolves, can accelerate the decomposition of sulphides (Evangelou & Setra, 1997), and

4) the formation of gypsum when calcium in the lime reacts with sulphate produced during sulphide mineral oxidation, may adversely affect soil drainage.

These problems can be overcome by using the Bauxsol™ technology, which has the added advantage of enhancing the nutrient retention capacity of the soil or mine site wastes thereby improving its suitability for plant growth (McConchie *et al.*, 1996, 2000a; Lin *et al.*, 2000). Bauxsol™ can be physically mixed with the sulphidic mine wastes, or it can be placed in layers within the column of sulphidic material, or it can be used to form subsurface PRBs (e.g. Figs. 4 & 5) that do not impede groundwater flow, or a combination of these strategies can be used (Titchenell & Skousen, 1996; Powell et at., 1998; Skousen et al., 1999). When PRBs are used to protect waterways near sulphidic waste piles from any acidic groundwater that may leach from the site, simple trenches dug parallel to the water course and back filled with a mixture of the excavated soil and Bauxsol™ will often suffice. Bauxsol™ application rates required for each site can be calculated to ensure that no acidic or metal-rich water can ever escape from the site and both laboratory and field trials show that the effectiveness of the Bauxsol™ technology is greater than theoretically expected although we are not yet completely sure why.

In large scale field applications involving application of the Bauxsol™ technology by direct addition of the mineral mixture to the sulphidic material, both the soil reaction pH and the groundwater pH were near neutral within 48 hours of completion of the treatment work and the treated wastes could be immediately planted as part of a revegetation programme (Maddocks, 2001). Ongoing testing shows that all leachates from sulphidic mine wastes treated using the Bauxsol™ technology are of acceptable quality and that the growth of grasses, shrubs and trees is excellent.
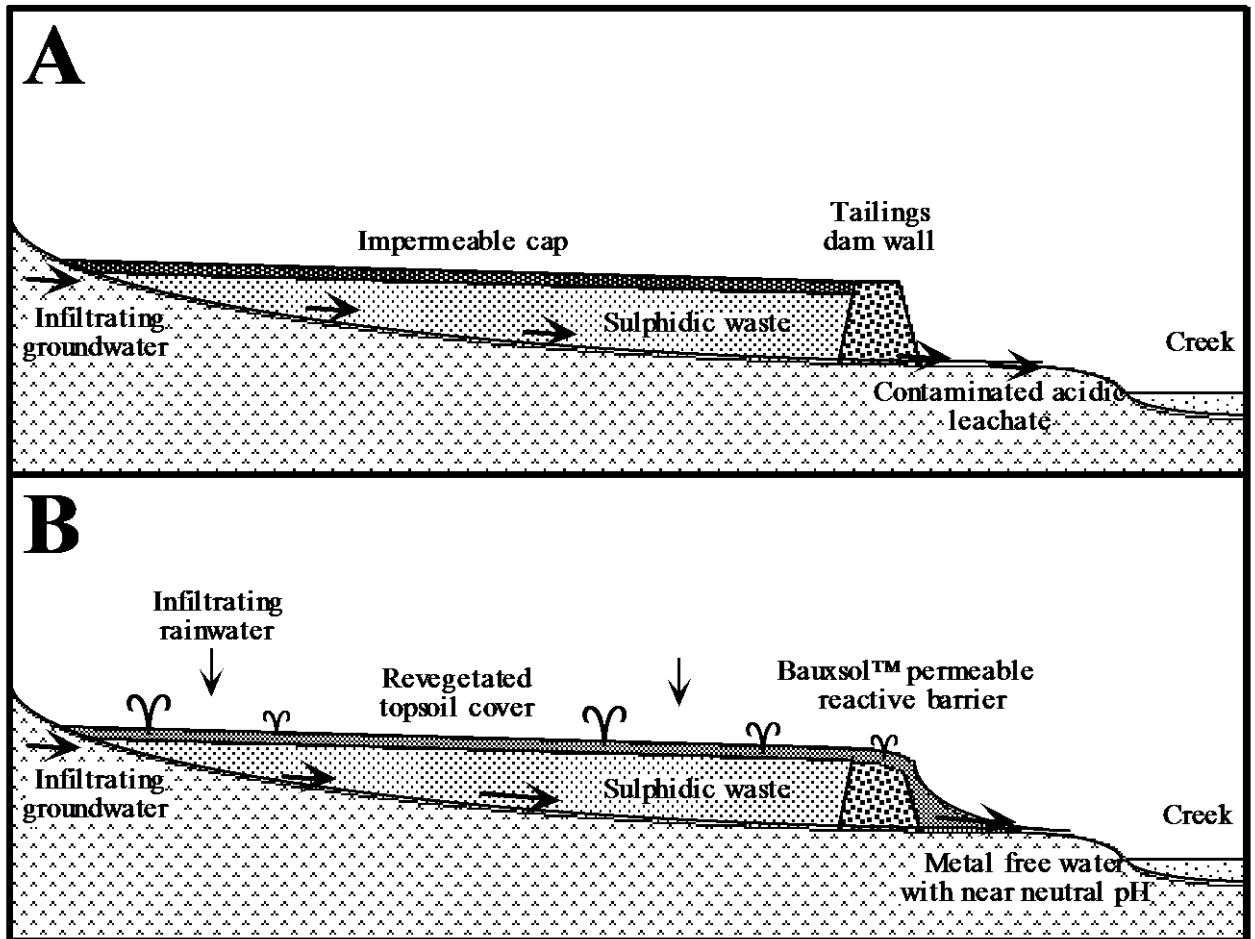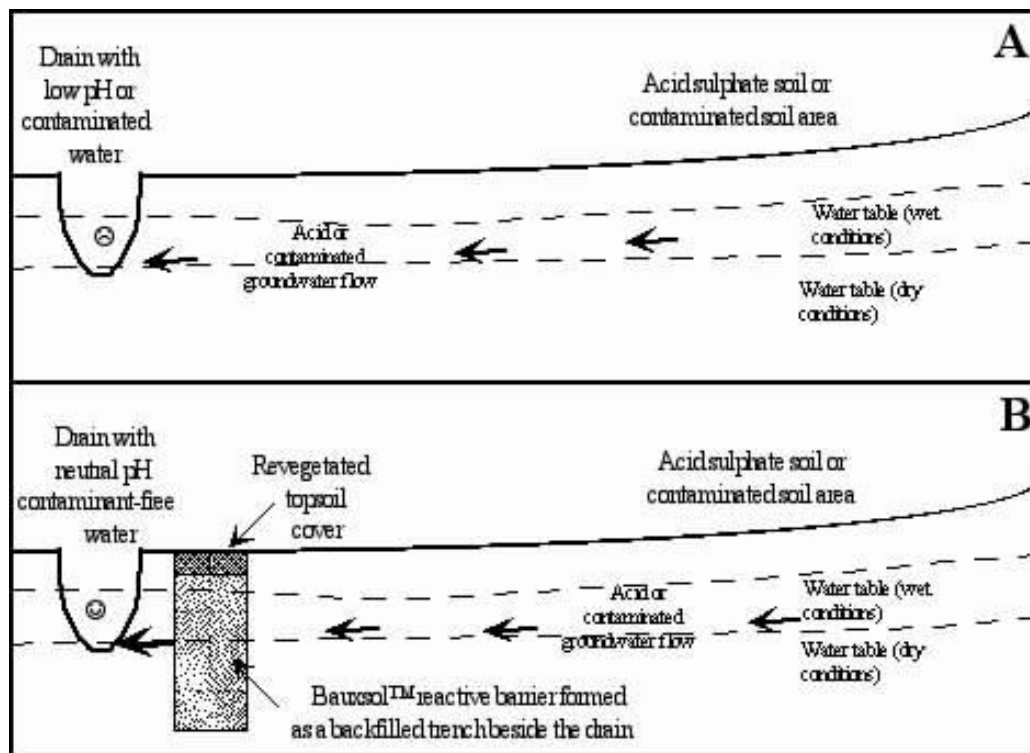
Figure 4. Use of a Bauxsol™ permeable reactive barrier to contain sulphidic mine wastes and avoid the need to maintain impermeable caps and linings. Additional barriers can be used within the waste dump if required and Bauxsol™ can be blended with the waste material near the surface to form an acid neutralising topsoil that can be readily revegetated.

In some situations, the same mass of material used in one application of the Bauxsol™ technology can be reused in another application thereby reducing the costs associated with both. For example, the residue remaining after treatment of AMD/ARD water can be reused in revegetation work elsewhere on the site, but an even more effective reuse strategy involves the use of the mineral mixture to remove phosphate from sewage effluent or abbatoir wastewaters and the reuse of this now phosphate enriched material to facilitate revegetation and leachate quality management required for rehabilitation of sulphidic mine wastes. The mineral mixture binds phosphate in a plant-available but non-leachable form and there is no loss of acid neutralising or metal binding capacity in the process. In one trial at a chicken processing facility, Bauxsol™ removed over 98% of the phosphate in digester effluent that had an initial phosphate content averaging 30 mg of phosphorus/L and 86% of this phosphorus remained plant available but not leachable (McConchie *et al*., 1999). Field trials have shown that the

nutrient enriched material promotes healthy plant growth and increases nutrient retention in degraded soils and mine site waste rock and tailings.


Figure 5. Use of a subsurface Bauxsol™ permeable reactive barrier to neutralize and decontaminate groundwater leachates in an acid sulphate soil area. The barrier is designed to treat the water passing through it, but not to impede groundwater flow.

Aberdare East Colliery Solids

The visual analysis of grain size of the coal samples at Aberdare East indicate that they are fine grained (<2mm) coal particles except for the sample taken from a cell wall where the grain size was on average 120mm and was mostly chitter. This indicates that the vast majority of the coal is slime from a washery operation and has a high surface area for oxidation reactions to occur. Because the vast majority of the sample is fine grained no corrections for grain size are required in calculating the Bauxsol™ technology addition rates (McConchie and Clark, 2003)

Sample pits allow the construction of a thessian polygon map (Fig. 6), which combined with the Vulcan Forge™ surface models for the surface contours, original ground, saturated and unsaturated fines allows the calculation of volumes; calculated volume estimates obtained for the washery waste are given in Table 1. During the sampling, 3 distinct layers were identified; capping, unsaturated fines and saturated fines. The "cut volume" provides an estimate of the error in each layer and is used to estimate the potential error; theoretically the

layers should not overlap and produce a "cut volume". Saturated fines are the volume of coal between the water table and the original ground layer (total volume of material between the water table and original ground * (1-porosity); Table 1).
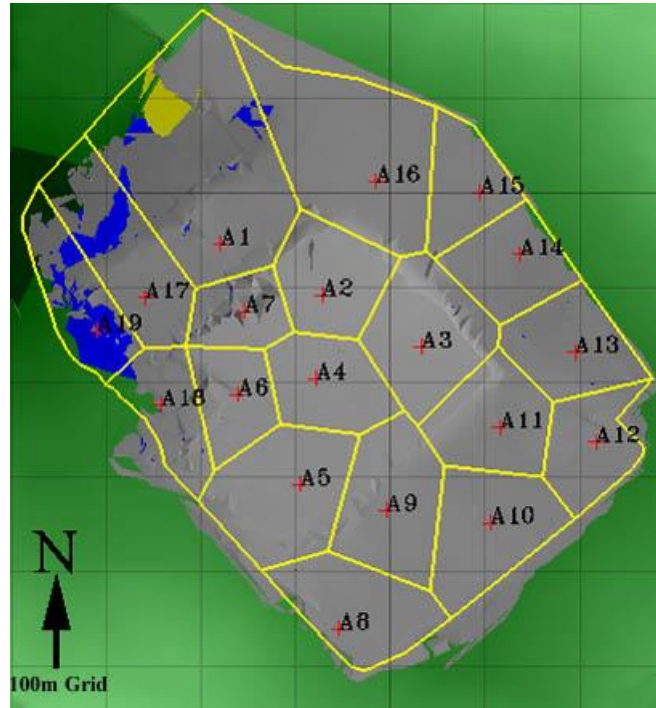
Figure 6. Thessien polygons constructed for the weighting of washery waste solid samples.

Table 1. The volumes of the different units in the Aberdare washery waste

Unit	Cut Volume m^3	Fill Volume m^3	Potential Error %
Capping	2461.0	184567.8	1.33
Unsaturated Fines	11049.2	720113.4	1.53
Saturated Fines	31491.1	337793.3	9.32
Total	**45001.3**	**1242474.5**	**3.62**

An acid base account of potential acidity from sulphides (TPA), the stored acidity (TAA) attained from the analysis of samples from the sampling pits, for each of the volume weighted layers (Table 1) provides the mass production of acidity (MPA; Table 2). Similarly the acid neutralizing capacity (ANC), or neutralisation potential (NP) for each of the volume weighted layers can be calculated (Table 2). The excess is then the difference between ANC and the MPA, where negative numbers indicate that more acidity can be produced than neutralized and the need to add further acid neutralizing materials.

Table 2. The volume weighted acid base accounting for the Aberdare East washery tailings.

| Total Sulphur ABA	Field Mass (t)	MPA tons CaCO3 equivalent	NP tons CaCO3 equivalent	Excess tons CaCO3 equivalent
Capping	300933.0	3216.56	5388.85	2172.29
Unsaturated Fines	799574.8	28212.41	13487.93	-14724.48
Saturated Fines	413459.0	20574.52	6308.29	-14266.23
Total	1513966.7	41933.2	25185.1	-16748.1

Data in table 2 indicates that only the capping material has any residual acid neutralising capacity, most likely by the adsorption of H^+ to clays, and that the tailings will be the sole source of acidity leaching from the area. Based on Table 2 the data would indicate that 4 times the Bauxsol™ would be required because it has only one quarter of the acid neutralising capacity of lime. However, other work (e.g. Clark 2000) indicates that the quantity of Bauxsol™ required for neutralisation of un-oxidized pyrite is not linear and that as sulphide percent decreases that the quantity of Bauxsol™ required also decreases but by a power relationship (Fig. 7). Consequently recalculating the components of potential acidity (un-oxidized pyrite) allows the calculation of both the liming rate and the Bauxsol™ addition rate (Table 3).

Table 3. Liming and Bauxsol™ requirements for the treatment of potential acidity at the site

Section	Field Mass (t)	CRS %	Lime		Bauxsol™	
			Rate kg /ton material	Required (tons)	Rate kg /ton material	Required (tons)
Capping	300932.96	0.0587	1.833	551.47	0.991	298.17
Unsaturated Fines	799574.78	0.4714	14.714	11 764.70	18.265	14 604.50
Saturated Fines	413458.96	0.3145	9.816	4 058.38	10.368	4 286.60
Total	1513966.7			16 374.55		19 189.27
Safety margin			200%	32 749.10	125%	23 986.59

The treatment requirements for the Aberdare tailings based on lime and Bauxsol™ are very similar, however, given the susceptibility of lime to leach during rainfall events it is likely that a safety margin of up to 200% will be required. However, experiments show that over the course of repeated 50mm rainfall events on lime at 1500 mm annual rainfall that 92% of the ANC is dissolved away, but for Bauxsol™ less than 5% of the alkalinity was removed. Consequently, for lime much higher safety margins are required and even at the safety margin stated there may well be a need to return and retreat the area after a few years. A safety margin for the Bauxsol™ should be no more than 125%, which coupled with the predictive graph

(Fig. 7) will mean that an effective Bauxsol™ treatment is possible, using about a third less material, than that predicted by acid base accounting for the tailing sulphide contents and the Bauxsol™ ANC.
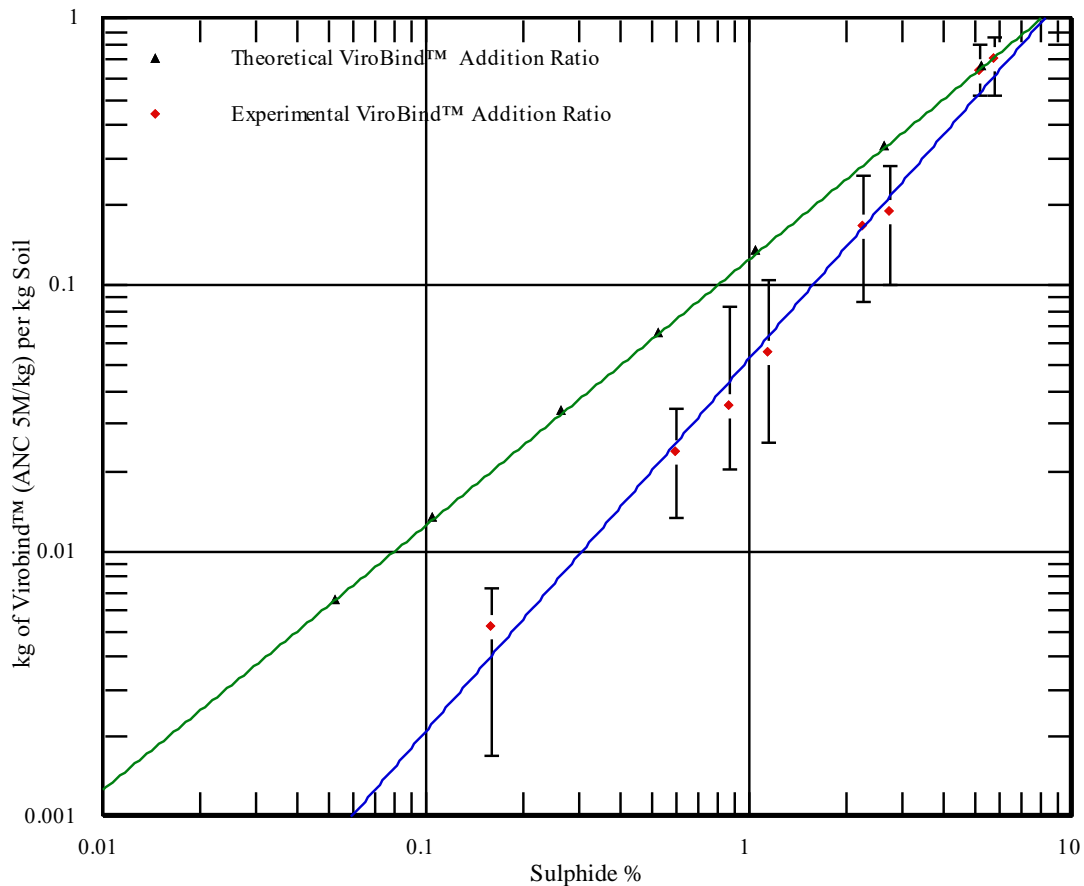
Figure 7. Graph showing the better than predicted capacity of Virobind™ at treating acid generated in materials with low sulphide contents.

Acid Rock Drainage Water Treatment Using the Bauxsol™ Technology

Acid mine drainage (AMD), or acid rock drainage (ARD), is a common problem wherever sulphidic waste rock or mine tailings are stored or otherwise exposed (Salomons, 1995; Evangelou, 1995; 1998). It affects most copper, lead, zinc, nickel, molybdenum, antimony, arsenic and silver mining and beneficiation operations, most gold recovery operations (other than those involving placer deposits), many coal mining and beneficiation operations, and others. AMD/ARD forms when sulphide minerals (particularly pyrite) are exposed where they can react with atmospheric oxygen and moisture to produce acid, metal ions and sulphate ions.

Some metal ions can later react to form low solubility metal hydroxides (e.g. the orange-brown precipitate seen in many areas affected by AMD/ARD) and release more acid in the process, and some may form meta-stable hydroxy-sulphate minerals (e.g. the yellow coloured

jarosite) that may later oxidize to release more acid (Bigham *et al*., 1990). The continual discharge of AMD/ARD water can have a cumulative or a chronic environmental impact, or both, but the greatest environmental threat is associated with the failure or overtopping of a dam containing the contaminated water because under these circumstances large quantities of contaminated water can be discharged very rapidly into nearby ecosystems. AMD/ARD is widely acknowledged as the greatest environmental problem facing the mining industry with serious impacts from both the acid and the metal ions. Preventing the formation and escape of these acidic metal-rich leachates from mineral recovery operations is both a management problem for modern mining operations and a major remediation problem for wastes associated with abandoned mining operations. Adverse environmental impacts can be avoided either by treating the AMD/ARD water or by preventing the formation of the acidic metal-rich leachates; however, once the AMD/ARD has formed there are few treatment options available and all involve some form of chemical treatment.

At sites where annual evaporation exceeds annual precipitation, management of ponded AMD/ARD has often relied on evaporation of the water, but this approach requires a dam large enough to hold all the water that could be accumulated during a series of high rainfall events. There is a permanent risk of dam failure or overtopping, and as water evaporates the concentration of contaminants in the remaining water progressively increases. This is the 'do nothing' option and in most countries it is no longer acceptable.

Ponded AMD/ARD water can be treated *in situ* or by pumping it to a chemical processing facility for treatment prior to discharge. There are many designs and operational processes available for chemical treatment facilities, but all involve substantial capital investment and ongoing operational costs. Facilities that incorporate final treatment by reverse osmosis can produce very clean water, but at a cost that is usually prohibitive. Sulphate reducing bacteria (SRBs) can be used to convert sulphate in the water to sulphide that can react with the metals to form insoluble metal sulphides, but there are problems with maintaining suitable bacterial populations, some metals (e.g. aluminium) don't form low solubility sulphides in water, and the metal sulphide sludge that is produced must be stored under anoxic conditions forever or separated and reprocessed to recover the metals and the sulphur. For some dam or pit lake waters, electrochemical techniques can be used to recover some metals (particularly copper) as a commercial resource, however, when used alone, this approach can not result in the production of water that is compositionally suitable for discharge. Treatment of AMD/ARD water within a containment dam is generally more economical, but conventional treatment by lime addition does not usually reduce metal concentrations to the low levels required for the

protection of aquatic ecosystems and the treatment results in the formation of large volumes of unstable sludge that is itself an environmental hazard.

Flowing AMD/ARD water is even more difficult to treat, particularly if flow volumes are high, and the do nothing option has been the preferred management strategy in the past (Salomons, 1995). Flowing water can be treated either by passing it through a permeable reactive barrier (PRB) or by diverting it to a containment dam or chemical processing facility for treatment (Titchenell & Skousen, 1996; Powell *et al.*, 1998; Skousen *et al.*, 1999). Diversion to a containment dam or chemical processing facility for treatment has the same problems as apply to the treatment of ponded water and the additional problem of having to treat and discharge the water at a rate equal to the rate of flow of water that requires treatment. The option of using permeable reactive barriers (PRBs) has the potential advantage that well designed barriers can be constructed and left unattended, but there are many problems with designing barriers that work effectively and for long enough. Designing PRBs that do not develop preferential flow pathways (piping or tunnelling) is difficult, but can be achieved, and the main problem lies with the selection of suitable reactive materials for use in the construction of the PRB. For extremely acidic water (pH < about 2.5), olivine-rich rocks can be used to form very cheap PRBs but they can not raise the pH or reduce the metal content of the water sufficiently and they can really only be used as a first stage treatment method. Limestone (or similar materials such as magnesite) has been widely used to form PRBs but there are many problems with its use (Evangelou & Zhang, 1995; Powell *et al.*, 1998; Evangelou, 1998) including:

1) Reaction between lime and sulphate forms gypsum that blocks pore spaces and progressively reduces the hydraulic conductivity of the barrier.
2) Aluminium- and iron-oxyhydroxides that precipitate as the lime neutralizes the acid commonly coat lime particles and prevent them from continuing to neutralize the water,
3) Lime is slightly soluble and can be leached out in high rainfall areas before all the acid has been produced, and
4) Lime barriers seldom reduce metal concentrations to acceptably low values.

Anoxic limestone drains (Titchenell & Skousen, 1996; Skousen *et al.*, 1999) were developed in an attempt to solve the problems caused by iron-oxyhydroxide precipitation, but they can not prevent aluminium hydroxide precipitation and they do not overcome the other problems associated with the use of lime; it is also very difficult to ensure that anoxia is

maintained in the drains. Many anoxic limestone drains fail within a few months of construction and very few continue to operate effectively for more than about 3 years.

The Bauxsol™ technology provides a cost-effective new alternative to existing methods for treating both ponded and flowing AMD/ARD water. It can be used both to neutralize the acid in the water and to strip metals from it so that it can be discharged safely and will not require indefinite storage; its performance is not affected by the salinity of the water. The ViroMine™ reagent can be added directly to ponded AMD/ARD water to treat it to the high standards required for the protection of aquatic ecosystems or to the less stringent drinking water, stock watering or irrigation water standards as required. The amount of reagent required, the blend to be used and the application strategy will depend on the initial composition of the water to be treated and the treatment targets adopted.

Use of the Bauxsol™ technology to treat ponded AMD/ARD is not limited by the volume of water to be treated and the results of treating large water bodies are consistently similar to the results obtained in laboratory studies of samples of water from the large body. However, in field applications, as opposed to laboratory tests, some additional treatment is usually needed to allow for stored acidity in near-surface sediment in the dam and any additional contaminated water that flows in while the treatment is in progress. When the Bauxsol™ technology is used to treat acid mine waters by direct addition, the cocktail of minerals that are added produces a thin sediment blanket on the bottom of the water body rather than the gelatinous sludge that is commonly associated with the use of lime. If the water from a dam or pond is completely discharged after treatment, the sediment residue remaining can be easily vegetated and will support healthy plant growth if some organic carbon and a source of phosphorus and nitrogen (e.g. biosolids from sewage treatment plants) is added.

The mixture of minerals that forms the basis of the Bauxsol™ technology can also be used to form permeable reactive barriers (PRBs) that will neutralize acid and strip trace metals from contaminated water without impeding water flow. The PRBs can be constructed using porous pellets or blocks prepared using the mineral mixture or by mixing the minerals with sand or locally available soil or crushed rock. The design and dimensions of each PRB need to be set to provide a balance between detention time (i.e. reaction time) in the barrier and the permeability required to handle the flow rate and volume of the water to be treated. PRBs designed to use the Bauxsol™ technology have several advantages over PRBs constructed using limestone including:

1) they can be used with fully oxygenated water,

2) iron and aluminium are largely removed by crystal growth on iron-oxides and aluminium-hydroxides in the mineral mixture rather than by precipitation of oxyhydroxide coatings on particles that need to remain in contact with the water,

3) gypsum is not formed and therefore does not adversely affect permeability,

4) the minerals in the mixture have a low solubility and are not lost during high rainfall,

5) metal concentrations in water that passed through Bauxsol™ PRBs are acceptably low, and

6) PRBs constructed using the Bauxsol™ technology will support healthy plant growth and can be vegetated while still in use.

Tests on PRBs constructed using the Bauxsol™ technology show that their permeability remains roughly constant from initial installation until the limit of their water treating capacity is reached. As with all PRBs, there is a limit to their capacity to treat water to the required standard and at that point they need to be replaced. However, unlike PRBs formed using limestone or other materials, metals bound to the minerals in PRBs constructed using the Bauxsol™ technology remain strongly bound and if the barrier material needs to be removed and replaced, it can be spread on land elsewhere on the site and vegetated. Alternatively, the exhausted material in the PRB may simply be left where it is and vegetated, and a new PRB can be placed beside it.

In comparative tests involving treating AMD/ARD water by direct addition of the mineral mixture and by passing it through a PRB created using the reagent minerals and clean river sand, the final metal concentrations are usually slightly lower when the PRB is used (c.f. Figures 4 & 5). However, irrespective of which procedure is used, use of the Bauxsol™ technology can produce near neutral water with a very low trace metal load that is suitable for the maintenance of healthy aquatic ecosystems.

Aberdare East Colliery Waters

The piezometers and other water sampling sites at the Aberdare East colliery allow the construction of a thessian polygon map (Fig. 8), which combined with the Vulcan Forge™ models for the surface contours, original ground, saturated and unsaturated fines, estimates of porosity for the saturated coal then allows the calculation of ground water volumes. For Aberdare East the overall estimate of ground water is 109,445 m^3, but the chemistry of this ground water varies greatly (Table 5). The entry point for ground waters into the tailings is the eastern corner (A12; Fig. 8) and exits through the north western face as a saline acidic metal-rich ARD (LS, FCB and CS; Fig 8, Table 5). Water from seepages on the north western face of

the tailings were collected and treated with lime $(Ca(OH)_2)$, magnesium oxide, a Bauxsol™ Acid B Extra™ C1T5 blend, and a Bauxsol™ Acid B Extra™ C5T5 blend; treatment results for these waters are shown in Table 6. The data indicate that the Bauxsol™ removes metals well below the guidelines for protection of aquatic ecosystems, and provides well buffered water that can cope with small additions of acidity further down stream (Table 6).
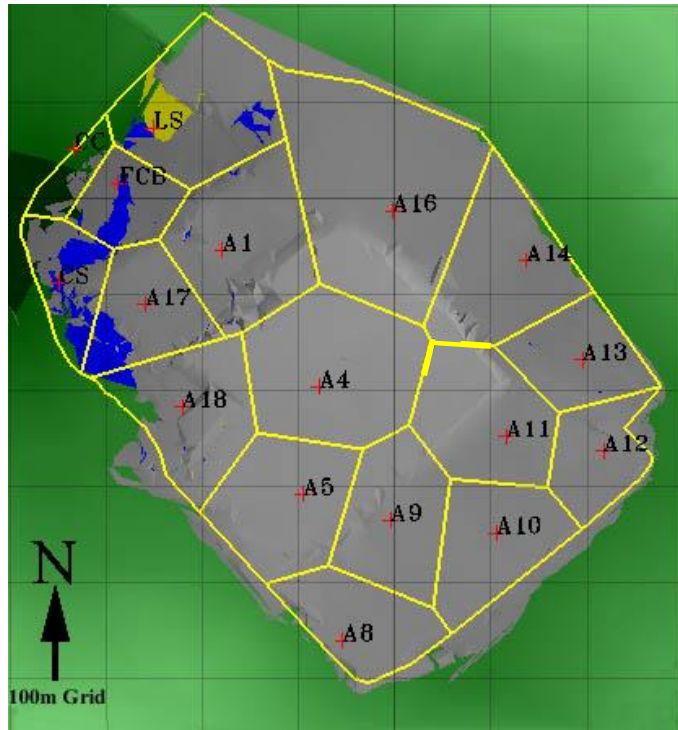
Figure 8. Thessien polygons constructed for the weighting of groundwater samples visually represented using Vulcan®.

Table 5. Summary of the geochemical variation for ground and surface waters sampled on site. Sample locations are shown Fig 8.

Site	Salts mg/L						Metals (mg/L)						
	Cl	Na	K	Ca	Mg	S	Cu	Zn	Fe	Mn	Cr	Ni	Al
Input	87	154	11.1	39.6	42.85	288.5	0.002	0.006	0.745	0.171	0.001	0.006	0.006
1	13.06	48.45	2.385	206.0	60.55	1033	0.051	2.046	26.52	10.91	0.001	0.629	14.78
4	48.12	76.45	17.20	137.0	50.35	1360	0.008	1.978	340.5	4.10	0.165	0.768	7.42
5	8.938	20.60	4.190	107	8.945	705.5	0.014	4.658	150.4	1.92	0.088	0.708	13.65
8	45.52	194.5	3.755	117	54.95	741.5	0.001	0.157	0.089	4.553	0.001	0.032	0.001
9	185	580	4.960	306.5	234.5	2905	0.004	0.575	89.19	12.63	0.001	0.257	0.796
10	10.83	63.85	11.95	526.5	66.80	1830	0.001	0.029	98.11	4.638	0.026	0.006	0.001
11	95.22	178	6.325	290	59.25	1060	0.001	0.024	1.437	2.917	0.001	0.040	0.001
12	191.2	568	10.9	450.5	217	2860	0.003	0.016	0.839	1.647	0.001	0.011	0.001
13	477	454.5	4.845	93.55	140.5	1355	0.004	0.305	38.39	5.685	0.001	0.301	4.041
14	637.6	957.5	10.24	251.5	205	2640	0.006	0.039	3.549	3.779	0.001	0.038	0.001
16	214.	301	0.826	266	123.5	2580	0.146	1.320	245.7	8.699	0.105	0.631	33.55
17	14.38	15.5	5.385	106.3	85.95	546.5	0.001	0.067	0.081	3.807	0.001	0.100	0.006
18	281.8	277.5	11.35	131.5	148.5	2085	0.017	1.049	401.6	4.281	0.167	0.606	13.3
CS	130.9	208	1.730	235	177	2580	0.001	1.063	295.5	10.2	0.205	0.877	41.78
LS	201	321	2.7	186	151	2450	0.001	0.805	188	8.045	0.112	0.425	89.1
CC	376.2	716	6.6	191	270	3210	0.001	0.253	204	6.880	0.036	0.169	34.5
FCB	488.1	1090	25.9	182	472	655	0.008	0.294	1136	11.86	0.587	0.347	1.906

Table 6. Treatment of the seepage water at Aberdare with, Ca(OH)₂, MgO, an Bauxsol™ Acid B Extra blends C1T5 and C5T5

Parameter	Initial Water Quality	Background[3]	ANZECC[1] Guidelines	Final Water Quality							
				Ca(OH)₂	Removal %[2]	MgO	Removal %[2]	C1T5	Removal %[2]	C5T5	Removal %[2]
Dosage g/L	0.000	~	~	0.951	~	0.834	~	5.500	~	5.123	~
EC (mS/cm)	3.85	1.27	00.5-1.5	3.71	~	3.56	~	3.79	~	3.9	~
pH	2.61	6.99	6.5-8.5	8.89	~	9.33	~	8.39	~	8.29	~
Acidity mg/L CaCO₃ eq	1879		~	0		0		0		0	
CO₃⁻² Alkalinity mg/L	0	0	~	0.3	~	0.8	~	0.3	~	0.3	~
HCO₃⁻ Alkalinity mg/L	0	35	~	62.5	~	52	~	53.2	~	53.2	~
Al (mg/L)	36.949	0.006	0.15	0.068	99.82	0.047	99.87	0.022	99.94	0.032	99.91
As (mg/L)	<0.001	<0.001	0.5	<0.001	n.c	<0.001	n.c	<0.001	n.c	<0.001	n.c
Cd (mg/L)	<0.001	<0.001	0.0002	<0.001	n.c	<0.001	n.c	<0.001	n.c	<0.001	n.c
Cr (mg/L)	0.008	<0.001	0.04	<0.001	>87.50	<0.001	>87.50	<0.001	>87.50	<0.001	>87.50
Cu (mg/L)	0.009	0.002	0.0025	0.006	35.70	0.006	35.03	0.001	88.88	0.001	88.88
Fe (mg/L)	168.255	0.745		0.001	100.00	0.001	100.00	0.001	100.00	0.001	100.00
Mn (mg/L)	9.249	0.171	3.6	0.344	96.28	0.533	94.24	2.948	68.12	2.313	74.99
Ni (mg/L)	0.653	0.002	0.017	0.018	97.22	0.030	95.36	0.010	98.47	0.008	98.77
Pb (mg/L)	<0.001	<0.001	0.0094	<0.001	n.c	<0.001	n.c	<0.001	n.c	<0.001	n.c
Zn (mg/L)	0.679	0.006	0.031	0.002	99.74	0.002	99.78	0.001	99.85	0.002	99.68
Cl (mg/L)	201.3	87		160.5		178.8		174.7		175.3	
Na (mg/L)	278	154		494		537		610		600	
K (mg/L)	1.65	11.1		131		52.1		69.4		60.3	
Ca (mg/L)	273.6	39.6	1000*	553		230		309		347	
Mg (mg/L)	237	42.85		224		455		352		330	
S (mg/L)	2772	288.5	1000*	3030		3160		2520		2660	

1. ANZECC (2000) guidelines for the protection of 80% of species;
    *ANZECC (2000) Livestock Drinking water Trigger Guidelines   [Fail] [Pass]
2. Negative removal percentages means a net gain
3. The water entering the site, assumed to be close to natural levels
n.c. = no change, NST= not sufficiently toxic

Is the Bauxsol™ Technology Environmentally Safe?

The minerals that form the basis of the Bauxsol™ technology are not known to pose any environmental hazard and leaching procedures result in only minor trace element release (Table 7). In practice, ViroMine™ reagents will trap and bind trace metals from most solutions that come in contact with it even if the trace element concentrations are in the low µg/L range. Although the matrix is composed of very fine grained minerals, they act as an excellent flocculant and are remarkably non-dispersive in water.

Table 7: TCLP stability of the treatments compared to the NSW EPA TCLP Inert Waste Guideline (NSW EPA 1999)

Metal	Raw Bauxsol mg/L	Ca(OH)2 mg/L	MgO mg/L	Acid B Extra C1T5 mg/L	Acid B Extra C5T5 mg/L	Inert Waste [1] mg/L
Ag	<0.01	<0.001	<0.001	<0.001	<0.001	0.5
As	<0.01	<0.001	<0.001	<0.001	<0.001	0.5
Be	<0.01	<0.001	<0.001	<0.001	<0.001	0.1
Cd	<0.01	<0.001	<0.001	<0.001	<0.001	0.1
Cr (total)	0.046	0.182	0.059	0.053	0.068	0.5
Cu	<0.01	0.051	0.022	0.011	0.018	No Limit
Hg	<0.01	<0.001	<0.001	<0.001	<0.001	0.02
Mo	<0.01	<0.001	<0.001	<0.001	<0.001	0.5
Ni	0.018	0.620	0.591	0.133	0.134	0.2
Pb	<0.01	<0.001	<0.001	<0.001	<0.001	0.5
Se	<0.04	<0.001	<0.001	<0.001	<0.001	0.1
V	0.055	<0.001	<0.001	0.059	0.063	No Limit
Zn	<0.01	0.082	0.061	0.031	0.043	No Limit

1. Inert waste TCLP limits (NSW EPA 1999)

Unlike lime, which often produces large volumes of unstable precipitate sludge, use of the Bauxsol™ technology results in the formation a non-dispersive sediment that supports healthy plant growth and from which it is very difficult to leach metals bound during water treatment. Whereas most metals removed by clays and zeolites are adsorbed and can be desorbed if chemical conditions change slightly, most metals bound by ViroMine™ reagents are held as structural components within the mineral matrix, are not exchangeable and can not be easily removed.

Sludge volume and settling rate experiments were conducted during the treatment of Aberdare East colliery waters. The results of these tests indicate that within 24 hour of the treatment addition to the column all solid material had settled. Lime treatment produced the

fastest settlement, and Bauxsol™ treatments settled the slowest, however, sludge volumes for the Bauxsol™ treated samples were about half to one-third that of the lime and magnesium oxide treatments (Figs. 9, 10 & 11; Table 8).

Bauxsol™ based treatments take slightly longer to settle when treating standing water, however, the volume of material remaining is considerably less. For a 5.5g/L treatment of the Aberdare East water with a Bauxsol™ Acid B Extra™ C1T5 blend, a sediment volume of 14.1 mL was obtained, whereas for 0.95g of hydrated lime 36.76 mL of sludge is produced, which is nearly 3 times the sludge volume for one 5th of the material added, or a 15 times greater sludge volume on a gram for gram basis.
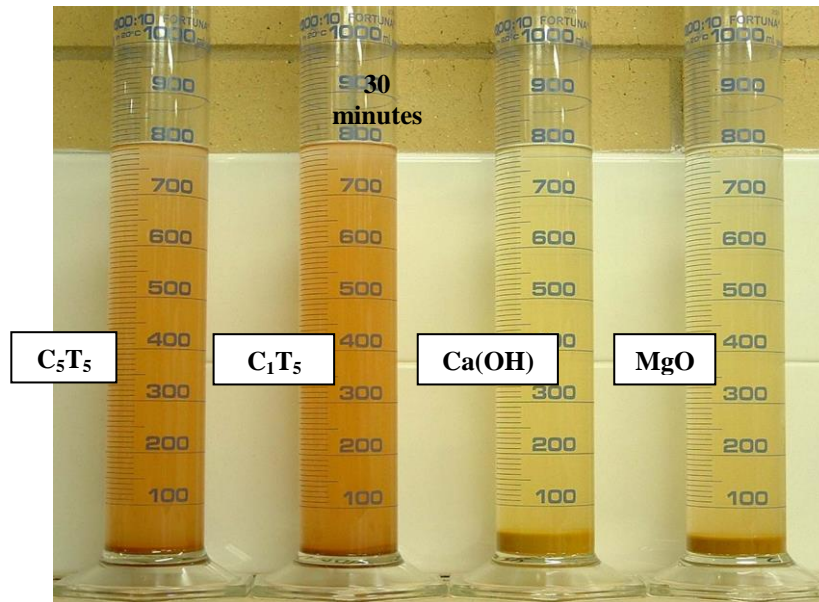

Figure 9. Suspended material and sludge volume after 30 minutes of settling (see Table 6 for dosing rates).
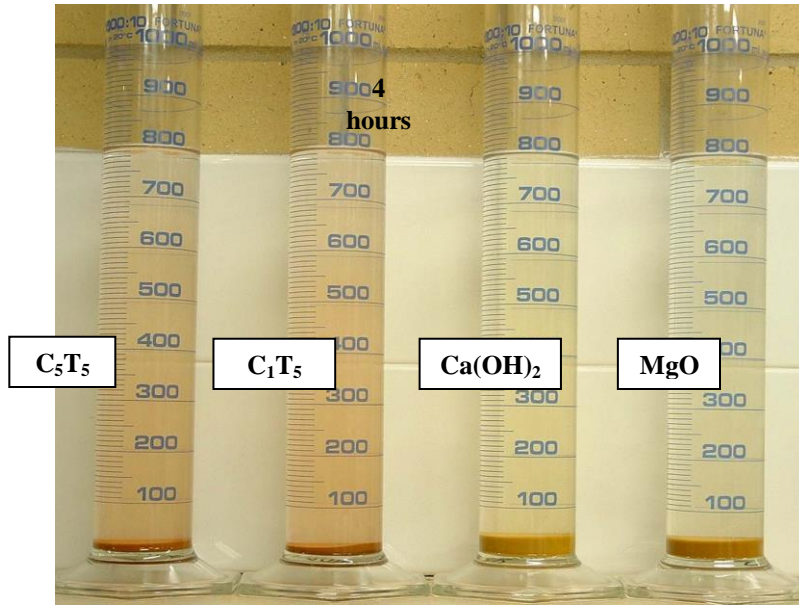
Figure 10. Suspended material and sludge volume after 4 hours of settling (see Table 6 for dosing rates).

Table 8. The residue volumes remaining after the treatment of seepage water

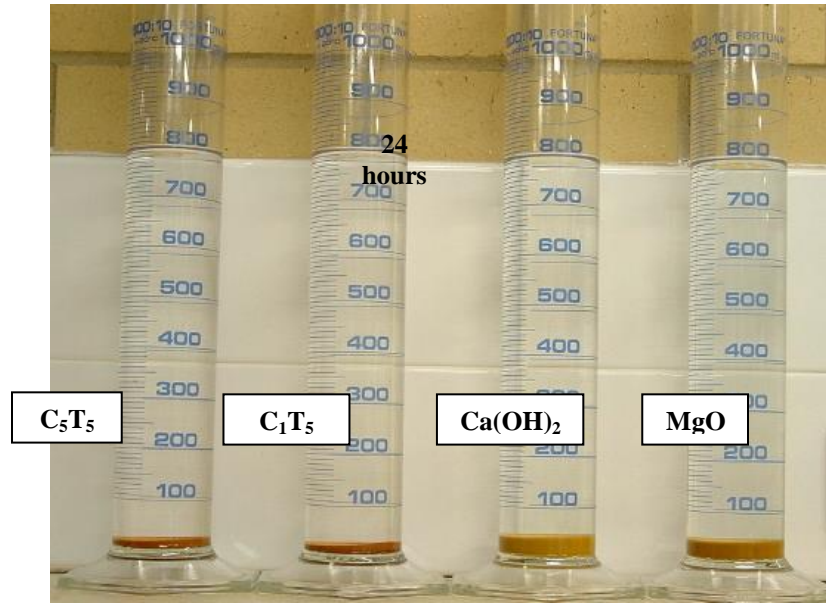| Blend	Dosage (g)	Volume / L of treated water				
		10 minutes cm^3	1 hour cm^3	4 hours cm^3	8 hours cm^3	24 hours cm^3
MgO	0.83	33.93	33.93	33.93	33.93	33.93
Ca(OH)$_2$	0.95	56.55	36.76	36.76	36.76	36.76
C1T5	5.5	9.90	12.72	12.72	12.72	14.14
C5T5	5.12	11.31	13.43	14.14	14.14	15.55

Figure 11. Suspended material and sludge volume after 24 hours of settling (see Table 6 for dosing rates).

How Does the Bauxsol™ Technology Work?

The acid neutralising capacity of Bauxsol™ is largely provided by low solubility alkaline minerals composed mostly of carbonate, hydroxide and hydroxycarbonate minerals, many of which react very slowly (McConchie *et al.*, 2000b). Hence, at least 48 hours are required for neutralization reactions to go to completion; tests involving the addition of standardized sulphuric acid show that about 40% of the acid neutralising capacity is used in 5 minutes, about 70% is used in 4 hrs and about 95% is used in 24 hrs (McConchie *et al.*, 1996).

The ability of the minerals to trap trace metals is also strongly time dependent and although most of the initial metal trapping is complete within 24 hours, metal trapping will continue, albeit more slowly, for many months and the longer the material is left the more tightly the metals are bound. Consequently, treatment time (the addition rate of the water treatment reagent) is an important consideration when using the Bauxsol™ technology and kinetic studies show that simply adding more of the reagent more quickly will seldom increase the rate of water treatment.

Although the exact mechanisms by which metals are trapped when the Bauxsol™ technology is applied are still being investigated, available data suggest that many trace metals are initially trapped by adsorption. This mechanism is particularly efficient because the material is dominated by particles with a high surface area to volume ratio and a high charge to mass ratio. However, adsorption alone can not explain the metal binding process because the cation exchange capacity

of the mineral assemblage is only about 3.7 meq/100g (e.g. 3.7 % of the total) and when desorption tests are run (using compulsive exchange reagents) on residue saturated with metals and aged for 7 days, less than 20% of the metals (less than 5% for As, Cd, Cr, Cu & Zn) can be recovered; recovery decreases as the material ages. Similarly, TCLP tests leaching at a pH of 2.88 are only able to remove a small proportion of the bound metals (Table 7) and this proportion also decreases as the metal-enriched residue ages. Furthermore, if metal enriched residue is left for a few weeks after use, it actually develops new capacity to trap metals (albeit, a very small, but measurable capacity) even if all available metal binding sites were occupied previously. Consequently, the data seem to indicate that elements, which may initially be bound by adsorption, are redistributed during aging to become structural components of low solubility minerals; part of the time dependence of metal uptake probably reflects the freeing-up of adsorption sites as initially adsorbed metals are redistributed. During treatment using the Bauxsol™ technology, many trace metals are also removed by direct precipitation and co-precipitation as the metals react with minerals in the treating reagent to form low solubility precipitates (particularly sulphates, carbonates, hydroxides and hydroxycarbonates) as the pH of the water being treated rises.

Residue Stability and Management

Accelerated aging experiments in oxidising conditions, show that the sediment remaining after treating metal contaminated water continues to hold bound trace metals and the longer the residual is left after use, the more difficult it becomes to remove the metals. Furthermore, as this residue ages, new metal binding sites become available, as a result of ongoing recrystallisation, and additional metals can be extracted from any new contaminated water that comes in contact with it. Metal saturated Bauxsol™ aged in an oxidising atmosphere at 60°C shows a substantial decrease in metal mobility by the TCLP leach with time (Fig. 12).

Similarly, if the residue remaining after water treatment using the Bauxsol™ technology is stored under reducing conditions, trace metal binding remains high except for aluminium, however even aluminium concentrations remain acceptable provided that the water pH remains between 6.5 and 8.5. Although the iron oxides and iron oxy-hydroxides in Bauxsol™ become unstable under highly reducing conditions, biogenic sulphides, which are readily produced in sulphate-rich water when the redox potential is low, provide a new metal trapping mechanism

that is effective for most metals except aluminium; and most metal sulphides have very low solubility. In laboratory trials that involved storing metal enriched residues in a nitrogen atmosphere at a redox potential below -300 mV (maintained by rotting oysters), sulphide production ensured that the concentrations of all metals in the liquid phase remained more or less unchanged over 3 months, except for iron which rose in concentration from less than 5 µg/L to about 150 µg/L. The results of TCLP tests run on the metal saturated residual over time indicate that metal mobility fell substantially after a few months of aging (Figure 13).
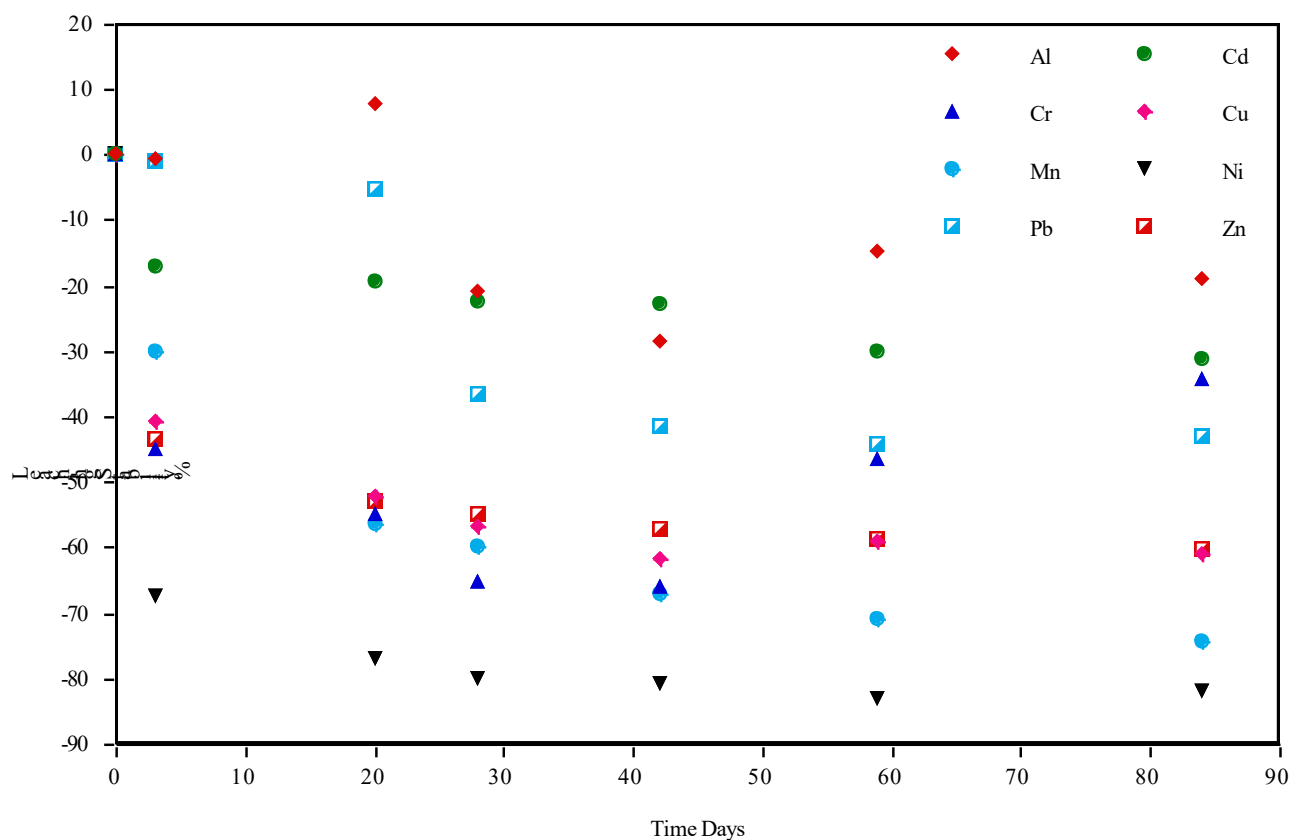
Figure 12. The 3 month trends in heavy metal mobility from Bauxsol subjected to accelerated (65°C) aging under oxic conditions (Eh >300 mV); positive values indicate an increase in mobility, whereas negative values indicate a reduction in mobility.
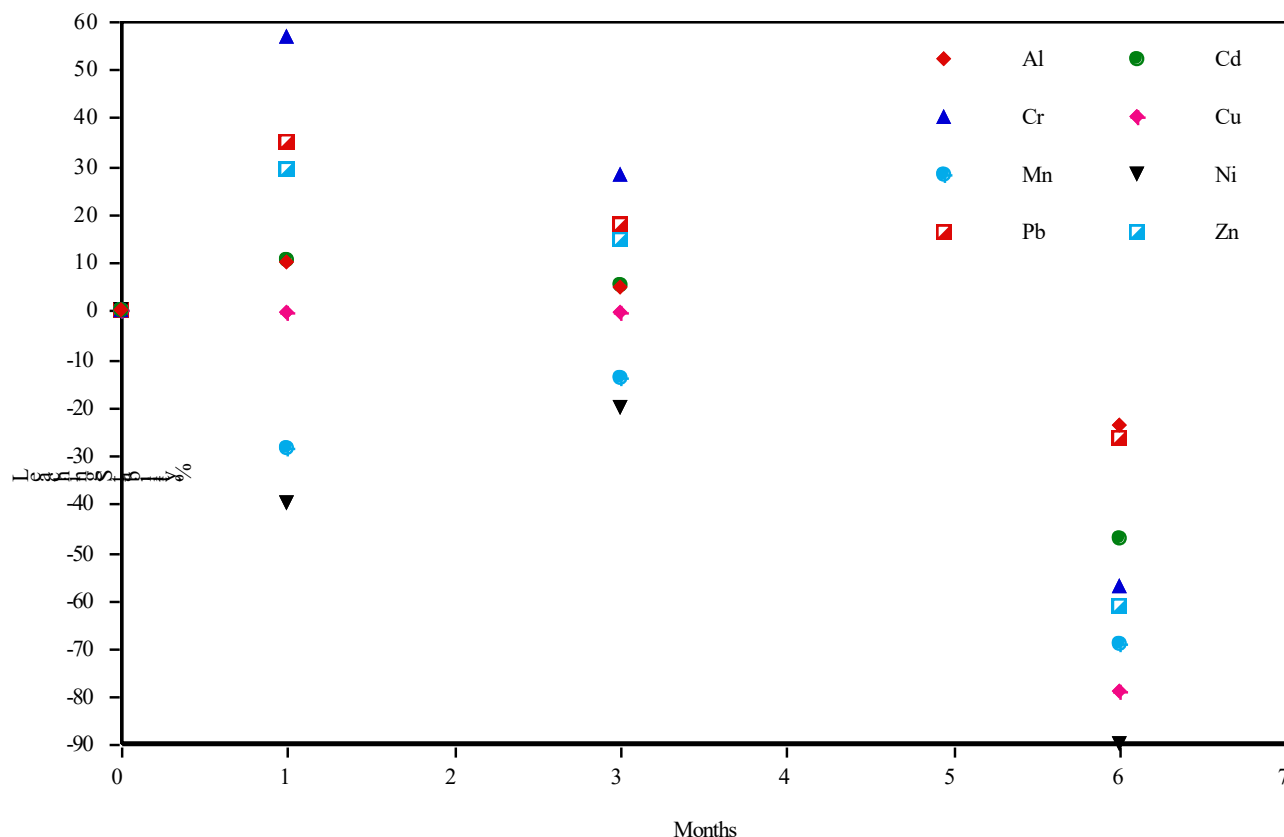
Figure 13. The 6 month trends in heavy metal mobility from Bauxsol subjected to anoxic-reducing conditions (Eh <-300 mV); positive values indicate an increase in mobility, whereas negative values indicate a reduction in mobility.

Based on all long term stability data it seems likely that some residue may be able to be reused to aid in the vegetation of highly degraded soils, waste rock or mine tailings. Previous studies have already shown that treatment with ViroMine™ reagents can facilitate plant growth on material scalded waste rock. In an extreme test of this potential, some additional Bauxsol™ was added to water treatment residual and mineral processing tailings exposed when the water level in the tailings dam at Mt Carrington was lowered after treatment, and mixed in with a rotary hoe. Three blocks with this mixture and an untreated control block were then planted with vegetables, fertilized and irrigated with treated tailings dam water. Within three months, all plants in the control block were dead whereas plants in the treated blocks were producing healthy crops and the trace metal concentrations in all plants remained well within the food safety limits for human consumption; silver beet growth was particularly impressive. Studies of plant growth and quality in the vegetable garden are continuing and the results will be reported in full during 2004.

Conclusions

Bauxsol™ technology provides and alternative solution for the treatment of ARD, and for the treatment of sulphidic mine wastes. The Aberdare East colliery, located in Cessnock, New South Wales, Australia contains impounded washery tailings that discharge substantial quantities of ARD. Investigations show that relatively clean water enters the south-eastern corner of the tailings and moves to the northwest down the hydrological slope, before exiting at the north western batter slope into a small creek. During the passage through the tailings salinity, metal content, redox potential, and temperature increases, and solution pH decreases. These tailing impoundments contains 109,445 m^3 of water, 337,793 m^3 saturated fines, 720,113 m^3 of unsaturated fines, and 184,568 m^3 of clay capping. Acid base accounting indicates treatment rates for the water of 5.123kg/m^3 of a Bauxsol™ Acid B Extra™ C5T5 blend is required (561 t) and that a further 24,000 t of Bauxsol™ ViroBind™ is required to prevent further acid generation. This compares favourably with lime where a treatment of 0.951 kg/m^3 for the water (104 t) is required, but due to the high solubility of lime 32,750 t would be required to prevent further acid production from the tailings. The benefits of the Bauxsol™ based treatments are lowered sludge volume productions during water treatment, an increased chemical stability of the residues and therefore greatly reduced disposal costs, and a reduced susceptibility to dissolution of the ANC from the soil/tailings profile. The low solubility of the Bauxsol™ acid neutralising minerals means that the need to retreat previously treated areas after 5 or 10 years is greatly reduced, which is quite common with lime treatments, consequently lower safety margins for the Bauxsol™ is required and a cost saving can be realized.

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