

*THE LONG TERM STABILITY
OF METAL-LADEN VIROTEC REAGENT*

PLATFORM TECHNICAL DATA SHEET



LONG TERM STABILITY OF METAL-LADEN VIROTEC REAGENTS

The reagents used in Virotec technology have several remarkable characteristics that make them ideal for environmental remediation on land and in water. They have an excellent trace metal and metalloid binding capacity and, equally importantly, elements that are bound when the material is used to treat contaminated water or soil are held very tightly and only a small proportion can be released, even if the solid residue is leached at a pH of 2.88 (TCLP procedure). Furthermore, the longer the spent Virotec reagents are left to age after use, the more tightly the bound elements are held. As the residue ages some new metal-trapping capacity develops.

Virotec's technology has gained acceptance for treatment of heavy metal laden waters including acid rock drainage and industrial waste waters. However, most leaching studies have dealt with recently used Virotec reagents that have been stored in well oxygenated conditions for no more than a few weeks. Hence, it is necessary to evaluate the performance of contaminant-laden Virotec reagents to determine long term stability and likely contaminant release under various geochemical conditions over periods of 20 years or more.

Results from the simulated aging of metal-laden Virotec reagents under oxic, anoxic, and anoxic-reducing conditions suggest that metals removed using Virotec reagents are increasingly occluded from the environment with time. The precipitation of insoluble sulphides, or low solubility carbonates, hydroxy-carbonates or hydroxy-sulphates and solid state diffusion process explain the observed decreases.

INTRODUCTION

Virotec reagents are typically dry red solid powders that are a byproduct of bauxite refining and consist of a complex cocktail of minerals that include: abundant hematite, boehmite, gibbsite, sodalite, quartz and cancrinite, minor aragonite, brucite, calcite, diaspore, ferrihydrite, gypsum, hydrocalumite, hydrotalcite, p-aluminohydrocalcite, and portlandite, and a few low solubility trace minerals. Virotec reagents, unlike seawater-neutralised red muds, are manufactured products, where the manufacturing can be manipulated to alter the mineral composition based on the salts used to convert soluble alkalinity to insoluble forms. The exact composition and geochemical character of the Virotec reagents depends on operational conditions in the alumina refinery, the efficiency of Virotec's Platform Technology Reagent their caustic recovery systems, the concentration and Ca:Mg ratio used for the alkalinity precipitation, and the type and quantity of additives used.

Virotec reagents have been used for the remediation of acid mine drainage because they have naturally high acid neutralising and metal binding capacities. The removal of metals from solutions by Virotec reagents has been well documented and it is clear that metal uptake is not a direct adsorption by cation exchange process because the amount of metal that can be removed from spent reagent by compulsive exchange methods is typically much less than ten percent of the bound metal. More astringent solutions (e.g. TCLP leaches) release a greater proportion of the bound metals, but this proportion remains small relative to the total mass of bound metals. These observations indicate that metal removal by Virotec reagents involves the precipitation of new low solubility minerals, isomorphic substitution, co-precipitation and solid state diffusion. During recrystallisation of these new minerals, metals may either be released from, or may be more tightly bound within crystal structures.

Metals may also be affected within the environment by both redox and pH conditions. Consequently, the behaviour of metals in an oxidising environment may differ substantially from their behaviour in an anoxic environment, or an anoxic-reducing environment. Anoxic environments, by definition, have no oxygen and are usually neither oxidising nor reducing, however, anoxic-reducing environments not only lack oxygen, but are also reducing (have a negative Eh). In anoxic-reducing environments metals may be reduced from high oxidation states to lower oxidation states that may be less (e.g. Cr⁶⁺ to Cr³⁺) or more (e.g. Fe³⁺ to Fe²⁺) mobile. However, where reducing conditions also allow the microbial conversion of sulphate to sulphide, many metals such as iron that may be more mobile in their lower oxidation state, readily become immobilised as metal sulphides. To sustain ongoing reduction (a gain in electrons) a good supply of organic carbon (reducing capacity) and low Eh conditions (reducing potential) are required; a biological mediator (e.g. reduction catalyst) is usually also necessary. Where reduction occurs, the pH of the solution tends to rise as bicarbonate is formed as a byproduct of respiration. Where high sulphate and reducible iron concentrations are present and Eh is sufficiently low, pyrite or other iron sulphides are commonly formed. The production of metal sulphides provides a good sink for metals because most metal sulphides are highly insoluble, but these metals and metalloids may potentially be released during any subsequent oxidation. Virotec reagents contain a high proportion of iron oxyhydroxides and if they are used to treat acid mine waters in deep pit lakes, they may be exposed to oxidising, anoxic and anoxic-reducing conditions as they settle, which may affect metal binding behaviour.

This paper details the release of metals from Virotec reagents that have been loaded and over saturated with metals from a standard solution and have been aged under accelerated oxidising conditions (elevated temperatures and open to oxygen), anoxic conditions (exclusion of oxygen) and anoxic reducing conditions (exclusion of oxygen and a strongly negative Eh).

METHODS

Metal Loading

Virotec reagents were allowed to react with a mixed metal (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) standard solution at a concentration of two mM for eight days (196 hours); the reagents were maintained in suspension for the full eight days using a rotary tumbler and then centrifuged. This process of suspension addition and centrifuging was repeated until all solids were in the centrifuge tubes. The Virotec reagent was then rinsed in Milli-Q water and recentrifuged to remove pore water metals.

Oxic Accelerated Aging

A small quantity of Milli-Q water was then added to the centrifuge tubes and they were sealed and placed in an oven maintained at 65°C to provide hot humid conditions that would allow recrystallisation and mineral diffusion process to occur. Three replicates were used and sampled at intervals over four months; sample times were at 0, 3, 20, 28, 42, 59 and 84 days.

Anoxic and Anoxic-reducing Conditions

Polyethylene drums were established as incubators for anoxic and anoxic-reducing conditions (Figure. 1); two anoxic drums and two anoxic-reducing drums. Seawater was used as a sulphate source for reduction and nitrogen used as a purging gas to replace dissolved oxygen. Metal-loaded Virotec reagent was hung in dialysis bags inside each drum on a frame such that water samples could be drawn, and Eh and pH probes introduced.

To maintain anoxia nitrogen was bled into each drum. For the two anoxic-reducing drums minced oysters, and mangrove sediment were placed on the bottom of the drum. The oysters provided a readily usable carbon source and some bacterial populations, whereas the mangrove sediments provided a source of sulphate reducing bacteria to initiate reduction and create the negative Eh conditions required.

Leaching of Metals

A subsample of aged Virotec reagent was taken and subjected to the standard pH 2.88 acetic acid extraction, which is the most astringent of the standard TCLP extracting fluids, to facilitate heavy metal release from the solids and to provide a constant extracting fluid for data comparison. Two further subsamples of the metal laden Virotec reagent, prior to accelerated aging, were digested to determine the total metal loads present. The total metal loads may then be used to calculate the proportions of the metal load that have been occluded during loading, and the proportions mobilised by the TCLP extraction. However because Fe and Al are major constituents of the Virotec reagent the total metal loads for these metals are not indicative of the quantities removed from solution during loading.



Figure 1 - Schematic cross-section of the anoxic and anoxic-reducing drums.

RESULTS

Metal Loading



A lead smelter.

Characterisation of the loaded Virotec reagent used in these experiments is provided in Table I, which shows that the removal percentages from the liquid to the solid are very high and provide substantial metal loadings on reagent substrates. However, the leachability of many of the metals from the Virotec reagent remains extremely low and, for some metals, a substantial proportion of the metals is even occluded from the Aqua Regia digest. The leach data in Table I provide the base values for comparison of subsequent data obtained for different aging conditions and the proportion of metals released is the proportion of this base data (see later Figures 2, 3 and 4). Consequently, positive values indicate an increase in leach susceptibility (e.g. metals have a less stable binding to the Virotec reagent), whereas negative values indicate a reduction in the leaching potential (i.e. metals have a more stable binding to the Virotec reagent).

TABLE 1. TOTAL METAL CONTENTS OF THE METAL-LADEN VIROTEC REAGENT (TIME ZERO).

	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Solution Concentration mg/L	54	226	104	126	110	112	114	414	130
% Removal from Solution	98	47	99	99	99	32	46	98	71
Virotec reagent loading g/kg	2.11	4.27	4.16	5.00	4.40	1.44	2.11	16.23	3.70
Aqua Regia leachable g/kg	89.67	3.41	2.54	2.75	147.08	1.35	1.65	7.88	2.39
pH 2.88 acetic acid buffer leachable mg/g	22.10	3.29	0.07	0.38	0.77	1.02	0.35	0.34	1.33
Resistant to Aqua Regia attack on loading	NA	0.86	1.62	2.25	NA	0.09	0.48	8.35	1.31
Resistant to pH 2.88 acetic acid buffer	NA	0.12	2.47	2.38	NA	0.33	1.28	7.54	1.06
% pH 2.88 Acetic acid buffer leachable of the loaded metals	NA	77	2	8	NA	71	17	2	36
% Occluded of the loaded metals (resistant to Aqua Regia)	NA	20	39	45	NA	6	22	52	36
% Aqua Regia mobile, pH 2.88 acetic acid buffer, resistant of loaded metals	NA	3	59	48	NA	22	61	46	28

Oxic Accelerated Aging

Data for the three replicate pH 2.88 acetic acid extracts are averaged, recalculated as a proportion of the initial loading data (Table 1) and plotted as a function of time (Figure 2). The data indicate that metal binding to Virotec's reagents increases with increased age and that susceptibility to the pH 2.88 acetic acid leach declines in the range of 25-80 percent depending on the metal concerned. Cadmium has one of the lowest reductions in leaching susceptibility at 25 percent, but nickel, has an 80 percent decline. These data indicate that as metal laden Virotec reagent is allowed to age under oxidising conditions there is a significant decrease in metal leachability.

Anoxic Aging

Data for the anoxic aging of metal laden Virotec reagent are presented in Figure 3. These data are an average of the two samples leached using the pH 2.88 acetic acid solution and are presented as a proportion of the values obtained from the initial leaching (Table 1). The data show that although there is a small initial increase in the susceptibility of metals to leaching, as aging continues, the susceptibility to leaching decreases.

Anoxic Reducing Aging

Data for the anoxic-reducing aging of metal laden Virotec reagent are presented in Figure 4. These data represent an average of the two samples leached using the pH 2.88 acetic acid solution and are presented as a proportion of the values obtained from the initial leaching (Table 1). The data show that although there is an initial increase in the susceptibility of metals to leaching, as aging continues, this susceptibility decreases markedly. The susceptibility to mobilisation is slightly greater for anoxic-reducing samples than for anoxic conditions, except for iron where susceptibility increased substantially by 6,000 percent, compared to anoxic aging (3,600 percent) and oxic conditions (140 percent). Clearly, the conditions within the anoxic reducing drums are such that there is a much greater transformation of the iron oxy-hydroxide than in either the anoxic or oxic conditions. However, the leach susceptibility for the other metals (e.g. Zn, Ni and Cd - see Figure 4) was less when compared to the anoxic conditions (Figure 3).

For example the leachability of zinc decreased from a 30 percent increase in leachability to about a 60 percent decrease in leach susceptibility.

TABLE 2. TOTAL ANALYSIS OF THE METAL-LADEN VIROTEC REAGENT ALL DATA IN G/KG

	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Initial Leach	89.7	3.41	2.54	2.74	147.1	1.35	1.65	7.88	2.39
Anoxic 1	88.4	3.26	2.49	2.61	150.0	1.26	1.41	8.04	2.48
Anoxic 2	85.9	3.67	2.42	2.81	143.3	1.35	1.60	7.69	2.36
Anoxic 3	89.2	3.17	2.56	2.52	148.9	1.22	1.49	8.17	2.86
Anoxic-reducing 1	89.3	3.70	2.47	2.84	148.8	1.31	1.60	7.99	2.60
Anoxic-reducing 2	90.7	3.97	2.44	2.89	152.0	1.44	1.72	7.99	2.71
Anoxic-reducing 3	89.1	3.59	2.47	2.72	148.6	1.26	1.56	8.07	2.54

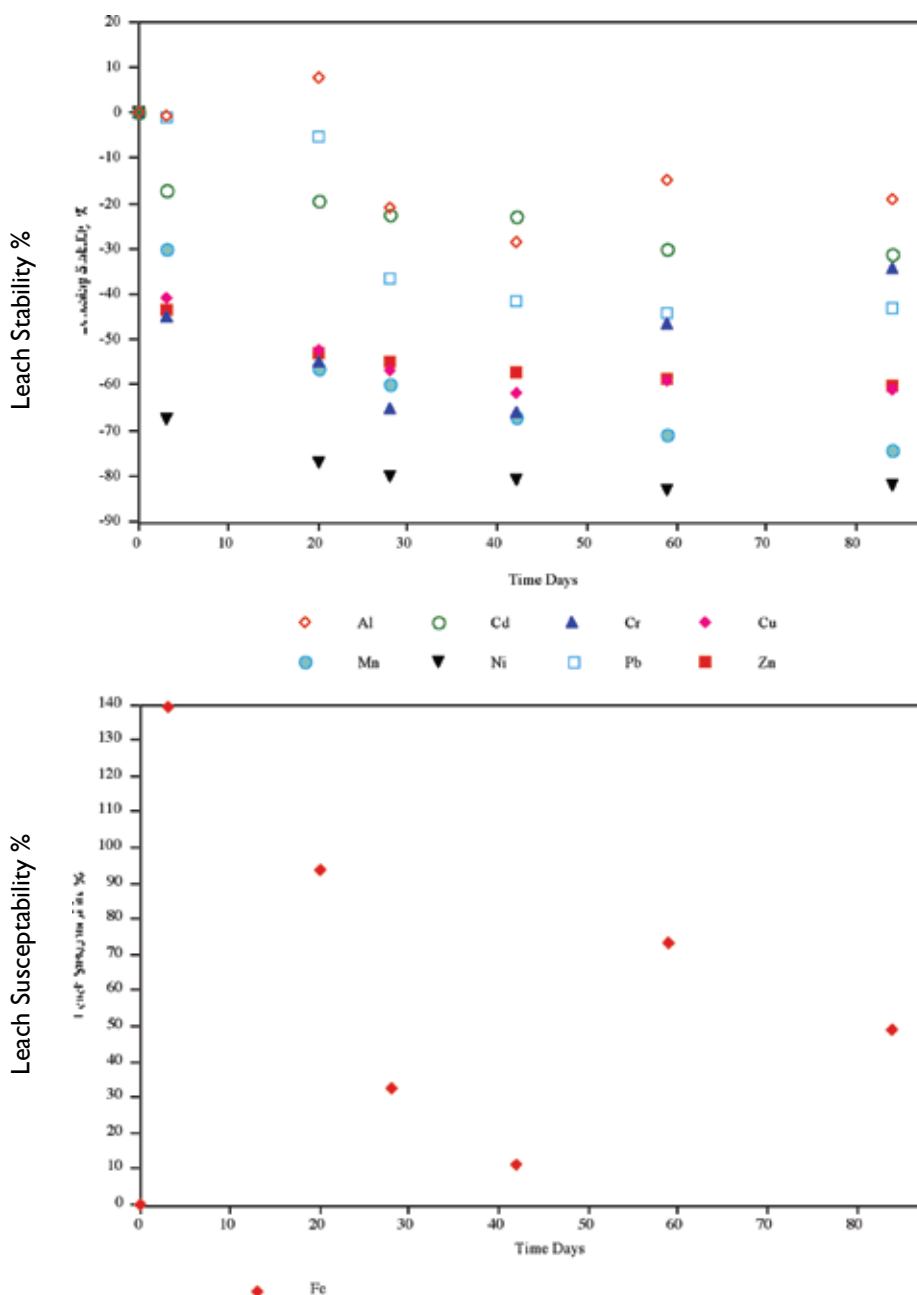


Figure 2. The proportional release of metals achieved using a pH 2.88 acetic acid buffer after removal to Virotec reagent and aging at 65°C.

TECHNICAL SUMMARY

The removal of metals from solution to mineral surfaces is highly complex, and although some may be readily leachable, others may be almost irreversibly bound. For Virotec reagents the removal of metals from solution appears to be mostly irreversible (Table I).

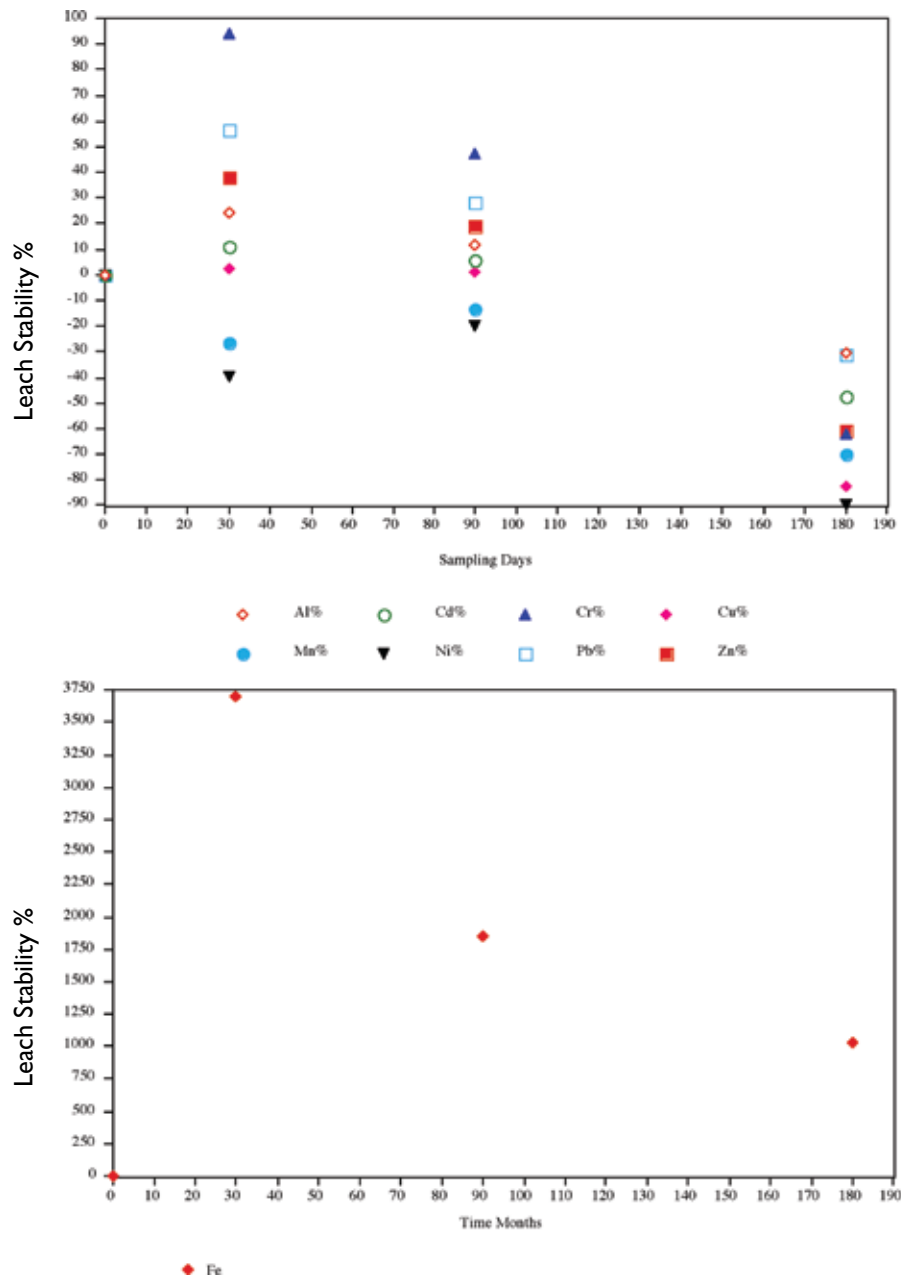


Figure 3. The proportional release of metals achieved using a pH 2.88 acetic acid buffer after removal to Virotec reagent and aging at $E_h > +0mV$ and $< +150mV$ anoxic.

Under oxic conditions some heavy metals may be irreversibly bound through oxide or oxyhydroxide mineral precipitation, whereas others may diffuse into the oxide or oxyhydroxide mineral structure under high concentration gradient conditions where they become difficult to remobilise. However, diffusive processes are slow compared to co-precipitation and precipitation processes, and are therefore unlikely to make a major contribution, unless the metal-loaded Virotec reagent is allowed to age for a long time. Metal removal from solutions occurs prior to any

recrystallisation and redistribution processes. The strongly decreased mobility of Ni, Mn, Zn and Cu and the smaller decreases for Cd and Pb mobility under TCLP leaching conditions shows that the recrystallisation process is occurring during the aging of Virotec reagent.

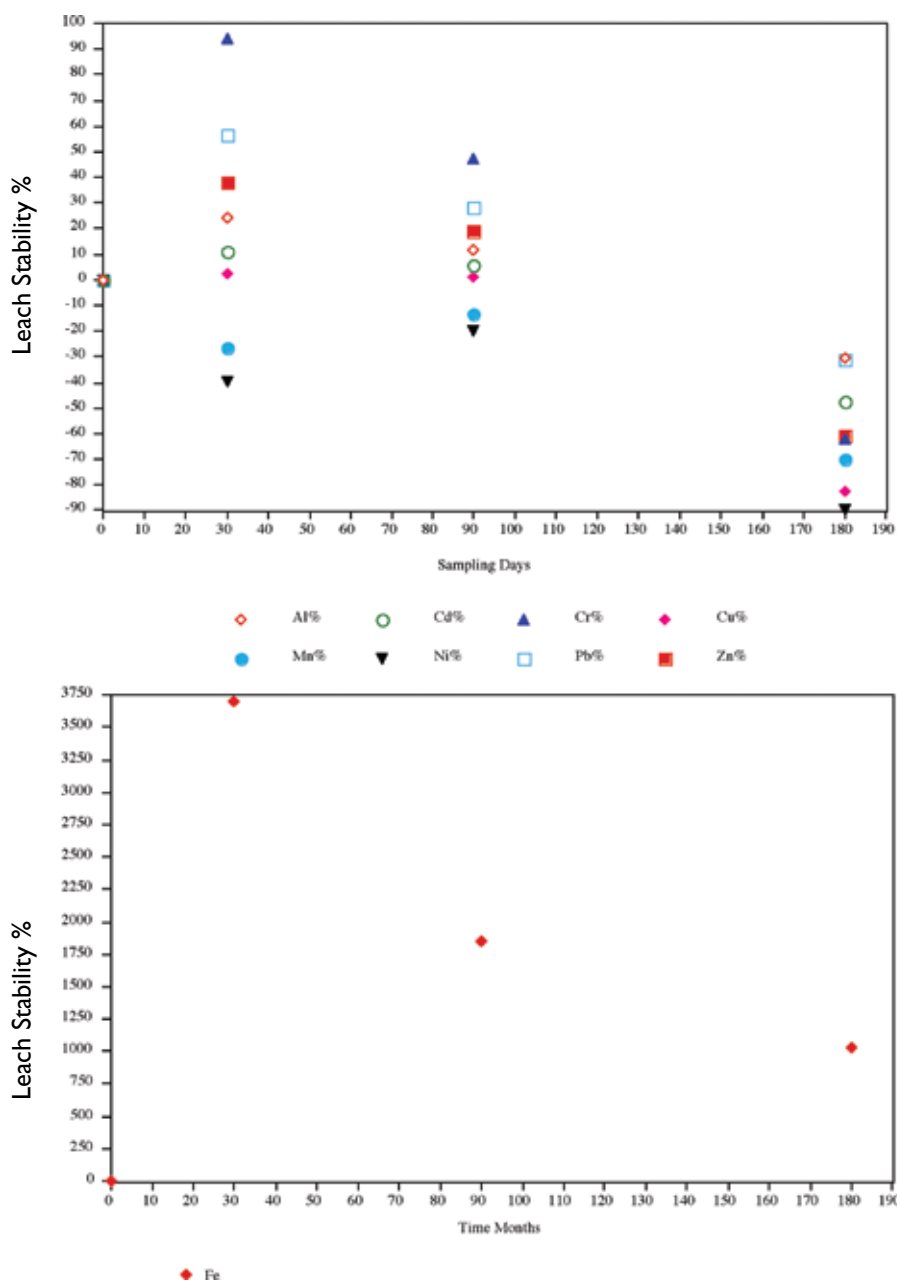


Figure 4. The proportional release of metals achieved using a pH 2.88 acetic acid buffer after removal to Virotec reagent and aging at Eh <-250mV in the absence of dissolved oxygen, with a dissolved sulphide (S²⁻) concentration >0.1 mg/L.

Several of the major acid neutralising components in Virotec reagent produced during the Basecon™ neutralisation process (e.g. para-aluminohydrocalcite, hydrocalcite and hydrocaluminite) have broad X-ray diffraction peaks, indicating that they are very fine grained and poorly crystalline. Such fine grained poorly crystalline minerals are susceptible to isomorphic substitution by other trace metals, and where crystal lattice structures are open, as they are for more amorphous crystal structures, metal substitution is more likely. Metals most likely to substitute into the aluminium hydroxy-carbonate structures are Cu, Zn and Co, although other metals including Ni, Mn, Fe and Cr may also be included. Metals that were coprecipitated with other oxyhydroxides may also form new more stable minerals during recrystallisation and hence the Virotec reagent increases metal removal to levels that are much greater than those associated with either the oxides, or the precipitated minerals alone.



Growth trials within one of the Gilt Edge Mine drums containing a waste rock and Acid B™ reagent mixture.

Although sulphide precipitation of heavy metals under anoxic-reducing conditions is recognised as a means of sequestering metals from the environment in an inert form, the metals only remain in this form if conditions remain anoxic. Mobilisation of metals as poly-sulphide complexes requires particularly strong reducing conditions. Given there may be some transformation of the Fe from the oxides into sulphides, the resistance of the high hematite concentrations present in Virotec reagents (30-35%) means that conversion to sulphides (e.g. pyrite) will be slow.

The storage of metal laden Virotec reagents under oxic, anoxic, and anoxic and reducing conditions shows the susceptibility to leaching of the bound metals decreases the longer that the Virotec reagent is aged. The ongoing diagenesis of the increasing irreversibility of metal binding to the Virotec minerals is through the recrystallisation of minerals from poorly crystalline forms to more crystalline forms, and or the diffusion of metals adsorbed on mineral surfaces in towards the core of the mineral crystal. Whatever the exact mechanism, the susceptibility of metals to leaching decreases over time and these on-going processes will reduce potential metal leaching to a point where bound metals may only re-enter the environment as part of the natural geochemical cycle.



Waste Rock Drum Trials at Gilt Edge Mine, USA

CASE STUDY

> Gilt Edge

The USA EPA has been conducting independent trials on ViroMine™ Technology Terra B™ reagent for the last five years. The trials are being conducted at the Gilt Edge Mine Site in South Dakota, USA. The results show the that ability of Terra B™ reagent to immobilise heavy metals increases over time.

Analyte (Units)	Control 2001	Result 2001	Result 2002	Result 2003	Result 2004
pH	1.93	7.9	7.96	8.35	8.62
Acidity (mg/L as CaCO ₃)	49,000	4	<5	<5	<5
Alkalinity (mg/L as CaCO ₃)	<LLD (5)	90	62	66	7
TDS (mg/L)	77,000	11,500	8,300	3,000	1,200
Sodium (mg/L)	9,300	2,970	2,990	570	250
Sulfate (mg/L)	55,000	6,000	5,800	2,200	840
Ag (ppb)	150	<(1)	1.1	<LLD (5)	<LLD (5)
Al (ppb)	1,200,000	<LLD (50)	10	66	<LLD (50)
As (ppb)	35,000	3.1	3.7	<LLD (10)	<LLD (10)
Cd (ppb)	630	0.41	0.4	<LLD (1)	<LLD (10)
Co (ppb)	2,200	1.5	11	<LLD (10)	<LLD (10)
Cr (ppb)	390	<(1)	12	<LLD (10)	<LLD (10)
Cu (ppb)	33,000	8.2	7.2	<LLD (10)	<LLD (10)
Fe (ppb)	21,000,000	<LLD (25)	18	120	210
Hg (ppb)	0.2	<0.1	0.2	<LLD (0.2)	<LLD (0.2)
Mn (ppb)	34,000	17	0.3	<LLD (10)	<LLD (10)
Ni (ppb)	1,600	2.1	1.4	<LLD (10)	<LLD (10)
Pb (ppb)	390	2.2	2.9	<LLD (10)	<LLD (10)
Sb (ppb)	500	<3.7	48	<LLD (10)	<LLD (10)
V (ppb)	1,700	<0.9	1.0	<LLD (10)	<LLD (10)
Zn (ppb)	29,000	42	21	<LLD (10)	<LLD (10)

Data for water leaching from sulfidic waste rock that had been treated using ViroMine™ Technology in the Trench Trial at the Gilt Edge Mine site; the data span the four years since the treatment was carried out. The control data were obtained for leachate emanating from the same type of waste rock that had not been treated with ViroMine™ Technology. < LLD indicates that the concentration is below the detection limit for the analytical procedure used (the detection limit is indicated in parentheses). NA indicates not analysed.

CASE STUDY

> Tasman Tannery

Tasman Sheepskin Tannery operates a waste water treatment system to remove chromium and suspended solids from waste water produced during the tanning process. The sludge is stored in a clay lined dam and is characterised by a very high total chromium content (around 5% total chromium or 50,000ppm) and a high leachable chromium content (between 30 – 40mg/L).

A large-scale study was conducted to determine the ability of ViroChrome™ reagent to immobilize chromium. Of particular interest was the long term stability performance of the ViroChrome™ reagent.

Numerous plots were treated with varying amounts of ViroChrome™ reagent to determine the optimum reagent addition rate. As shown below in Figure 5, chromium binding in Tasman Tannery sludge was time related, with TCLP results improving over time (in this case over a year) with no further addition of reagent.

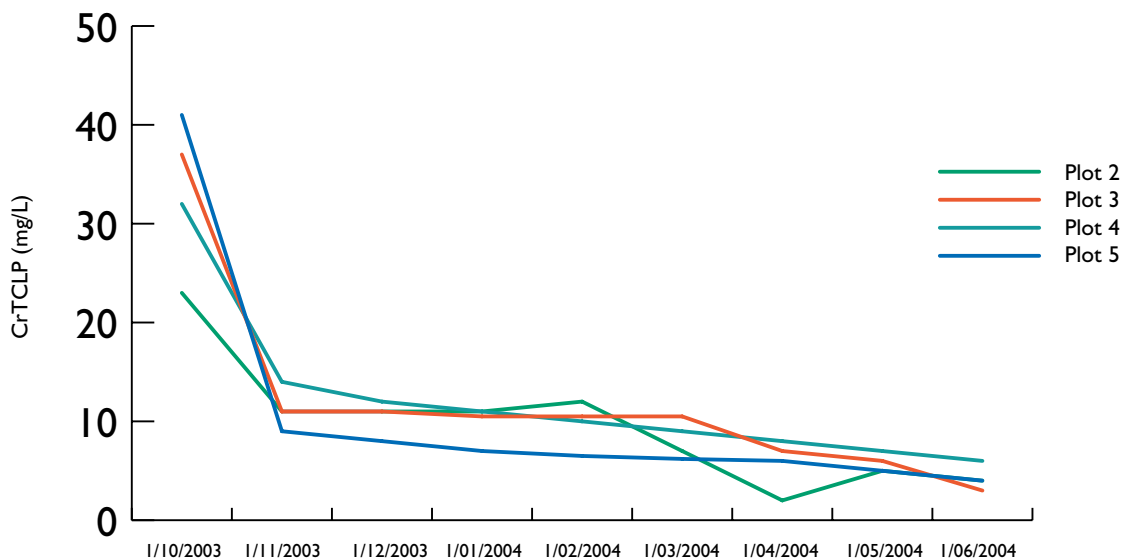


Figure 5 – TCLP Chromium verse Time, for various additions rates of ViroChrome™ reagent.