International Journal of Multidisciplinary Research and Development

Lee C Fergusson
Principal Researcher, Prana World Consulting, PO Box 1620, Oxenford, Queensland 4210, Australia.

A Field Trial to Engender Micro-concentrations of Lead (II) Using a Novel Sorbent in Highly Acidic Industrial Waste water at a Smelter Site in Derbyshire

Lee C Fergusson

Abstract

This study examines the relationship between extreme acidity and heavy metals (with a primary focus on lead) in industrial wastewater and the role of chemical reagents derived from alumina refinery residue to neutralize acid and reduce heavy metals to micro-concentrations (i.e., less than 150 µg/L) at a lead smelter in Derbyshire, England. The role of alumina refinery residue reagents in reducing the need for added flocculants and coagulants is also investigated. During the field trial, influent pH to the smelter's wastewater treatment plant averaged 1.7, with lead concentrations of 4.2 mg/L, cadmium concentrations of 8.7 mg/L, and zinc concentrations of 49.7 mg/L.

As a result of adding two chemical reagents at a rate of 0.25 g/L to Tanks 1 and 2 in the wastewater treatment plant, pH increased to an average of 9.5, lead concentrations decreased to 0.11 mg/L (a 96% reduction), cadmium concentrations decreased to an average 0.05 mg/L (a 98% reduction), and zinc concentrations decreased to 0.05 mg/L (a 99% reduction), all of which were under the 150 microgram target established for this trial. These post-treatment acidity and metal concentrations were within acceptable consent limits imposed by the UK's Environment Agency for discharge to the local receiving environment, and other floccing and coagulating agents, normally used during routine wastewater processing at the site, could be discontinued during the trial.

Keywords: Lead; acidity; wastewater; flocculant; coagulant; alumina refinery residue

Introduction

For much of the last 40 years, the health and environmental risks associated with lead have been highlighted and well documented by environmental scientists and health professionals (Agency for Toxic Substances and Disease Registry, 1999; [1] Gartley, 2002; [18] World Health Organization, 2012) [34], with lead mining, smelting and processing among the primary sources of contamination (Taylor, 2012) [30]. In both mining and other industrial activities, lead commonly features as a heavy metal of concern, particularly in relation to industrial wastewater but also in the context of emissions, contaminated soil and industrial solids treatment, due to its acutely toxic properties (National Health and Medical Research Council, 2014) [23].

The range of potential medical disorders associated with lead toxicity and poisoning is remarkable by any standard, and has been the subject of medical research for several decades. These potential disorders include adverse conditions related to: the central nervous system (e.g., cerebral palsy, convulsions and a number of different types of brain disease) and the peripheral and autonomic nervous systems; growth and human development, such as delayed neurological development in children and osteoporosis in later life; cognitive development, including reduced intelligence and learning difficulties; behavior, including violent and aggressive behavior, hyperactive behavior, school absenteeism and lethargy; hearing impairment; sight, including retinal degeneration; movement and muscular problems, such as motor dysfunction and paralysis; digestive disorders; renal failure; reproductive abnormalities, including chromosomal anomalies; and death (Bellinger, 2007; Brashear *et al.*, 1978; Campbell & Auinger, 2007; Fischbein, 1992; Lustberg & Silbergeld, 2002; National Research Council, 1993; Needleman, *et al.*, 1996) [2, 6, 7, 13, 21, 24, 25].

The removal of lead from industrial wastewater is typically effected by the addition of chemical agents such as calcium hydroxide (or "lime", $Ca[OH]_2$), magnesium oxide (MgO) or sodium hydroxide ($NaOH$). For example, Rao and Raju have shown at a lead-acid battery manufacturing plant in India that the separate additions of both $Ca[OH]_2$ and $NaOH$ neutralized acid and reduced soluble lead from wastewater at a pH of 8.0 (Rao & Raju, 2010). However, relatively large doses of each chemical were required to achieve significantly high enough levels of lead removal (e.g., >15.0 g/L of $Ca[OH]_2$ was required to reduce lead to >99% efficiency), and these

Correspondence
Lee C Fergusson
Principal Researcher, Prana World Consulting, PO Box 1620, Oxenford, Queensland 4210, Australia.

additives also generated an inordinate amount of "metastable" sludge, which in itself is difficult to treat and manage representing as it does a transfer of lead from the liquid phase (i.e., wastewater) to the solid phase (i.e., metastable sludge). Environmental research studies by Katsou, *et al.* (2011) [19], Khaoya and Pancharoen (2012) [20], Singanan (2011) [29], and Teekayuttasakul and Annachhatre (2008) [32] provide but a few recent examples which examine the presence and removal of lead from industrial wastewater using innovative methods.

Katsou, *et al.* (2010) investigated the combined use of ultrafiltration with mineral additives in the pre-treatment of wastewater containing high concentrations of lead. This study controlled for variables such as initial concentrations of lead in the wastewater, influent pH, membrane pore size, mineral type and concentration, and mineral-to-metal contact time. The authors showed that the dominant lead removal mechanism in ultrafiltration at a pH of 6.0 was precipitation (i.e., as a result of lead binding with other elements in the wastewater to form new chemical compounds, such as lead chromate [$PbCrO_4$], which formed insoluble precipitates retained by ultrafiltration membranes), although mineral adsorption enhanced lead removal. Thus the combined use of ultrafiltration and mineral additives was the most effective method for removing lead from wastewater, resulting in treated effluent that could be further treated biologically or could be discharged to the municipal sewerage system.

Khaoya and Pancharoen (2012) [20] also investigated the relationship between lead(II) and industrial wastewater, this time examining the role of hollow fibre supported liquid membranes (HFSLM) to extract lead from wastewater generated at an automotive battery manufacturer in Thailand. Like the work of Katsou *et al.* but unlike many other types of industrial waste research, this study controlled for a variety of factors, including both organic and "stripping phase" concentrations of lead (i.e., elemental lead in wastewater, as well as lead concentrations in so-called "stripping solutions", which included di-(2-ethylhexyl)phosphoric acid [$(C_8H_{17}O)_2PO_2H$], sulfuric acid [H_2SO_4], and kerosene), influent pH, and volumetric flow rates of both contaminated influent and stripping solutions. After providing an extensive analysis of the theoretical principles of HFSLM, and when controlling for these variables, the authors maintain that HFSLM was optimally effective in reducing lead at greater than 97% efficiency.

Singanan (2011) [29] maintains that the removal of lead (II) from industrial wastewater remains a major environmental challenge in industrialised countries. His novel study examined the role of activated biocarbon in removing lead from industrial wastewater in India, finding that biocarbon activated with powder produced by drying and grinding the plant *Tridax procumbens* (commonly called "coat buttons" or "tridax daisy") significantly reduced concentrations of both lead and cadmium in wastewater. Similarly, Teekayuttasakul and Annachhatre (2008) examined the removal of lead from sulfate-rich wastewater through biological sulfate reduction with hydrogen as an electron donor. In this experiment, sulfide was converted from sulfate by sulfate-reducing bacteria (SRB) in a gas-lift reactor and resulted in the reduction of lead as a lead sulfide (PbS) precipitate from 2,600 mg/L to 200 mg/L at a pH of 8.0. Furthermore, the toxicity of the wastewater before and after treatment also indicated that lead toxicity was reduced by 92% when using the so-called whole effluent toxicity (WET) test.

In each of these studies, influent pH was highlighted as critical to the outcome because pH controls lead removal from liquids and has been identified as one of the most relevant factors in both the biosorption and precipitation of lead from industrial wastewater. Most research has found, for example, that a pH of around 4.5-5.0 is optimal for the biosorption of lead because at pH above 6.0 biosorptive reactions decreases significantly. However, the reverse is true for precipitation: at a pH greater than 6.0, lead precipitates as a hydroxide, but at a pH under 6.0 lead precipitation is significantly reduced (e.g., Singanan, 2011) [29]. Khaoya and Pancharoen (2012) [20] found that a pH of 3.0 was optimal in the removal of lead when using stripping solutions and Mengistie, *et al.* (2008) [22] found that adsorption was optimal with a starting pH of 4.0, however, most research into the relationship between lead and industrial wastewater has been conducted on slightly acidic (4.5-6.5) or neutral pH liquids (e.g., Ho, 2005; Katsou, *et al.*, 2010; and Teekayuttasakul & Annachhatre, 2008) [16, 32] particularly when the biosorption of lead is utilized or when SRB are harnessed to precipitate lead.

Of the chemical reagents used in the last 15 years to remove lead and other heavy metals from industrial wastewater, among the most significant are those from alumina refinery residue (ARR, sometimes referred to as "bauxite refinery residue" or "red mud"); these types of reagents are typically referred to as being derived from "modified alumina refinery residue" (MARR) because the base ARR from which they are developed has been treated using one of a variety of chemical conversion methods designed to transform the raw residue from a highly caustic material with a pH >12.5 to a benign substance with different (and valuable) chemical and physical properties.

[The solid MARR referred to in this paper is a byproduct of the refining process where alumina (Al_2O_3) is extracted from bauxite using the Bayer Process (Habashi, 1995) [15]; the modification process involved added calcium- and magnesium-based salts to ARR in order to reduce sodium (Na) concentrations and hence the total alkalinity and causticity of the residue. Other alumina refining processes, including sintering and leaching, do not yield the same properties of base ARR and are therefore generally not considered viable when contemplating the application of MARR in environmental science or remediation.]

MARR has several unique chemical and physical properties of relevance to this study. For example, MARR is composed of a cocktail of metals and minerals, including the following major compounds in approximate descending order by volume: hematite (Fe_2O_3) at about 40%; beohmite (y-AlOOH) and gibbsite (Al[OH]$_3$) at about 25%; sodalite ($Na_4Al_3Si_3O_{12}Cl$) at about 10%; anatase (TiO_2) at about 4%; and minor compounds in approximate descending order by volume: aragonite ($CaCo_3$); brucite ($Mg[OH]_2$); diaspore (ß-$Al_2O_3.H_2O$); ferrihydrite ($Fe_5O_7[OH].4H_2O$); gypsum ($CaSO_4.2H_2O$); hydrocalumite ($Ca_2Al[OH]_7.3H_2O$); hydrotalcite ($Mg_6Al_2CO_3[OH]_{16}.4H_2O$); and para-aluminohydrocalcite ($CaAl_2[CO_3]_2[OH]_4.3H_2O$). The relative percentages of these compounds in MARR depend mostly on the properties of the original bauxite ore and operational processes at the refinery, which together can dramatically affect final ARR properties.

Three observations relevant to this research can be made from this data on MARR. First, the presence of hydroxides and oxy-hydroxides in MARR contribute significantly to its acid neutralizing capacity (ANC). For example, the three hydroxides in gibbsite, sixteen hydroxides in hydrotalcite, seven oxy-hydroxides in ferrihydrite, and four hydroxides in p-alumunohydrocalcite collectively contribute significantly to

ANC. The ANC of both ARR and MARR has been the subject of a significant amount of prior research (e.g., Rubinos et al., 2011) [27]. Studies have indicated the ANC of MARR is about 3.6 mmoles of acid/kg at pH 8.0, but can be as high as 17.0 mmoles of acid/kg at pH 5.5, but with the addition of other acid-neutralizing chemicals like MgO, ANC can be adjusted upward even further.

Second, the complex of many differently charged particles in MARR together cause long-term isomorphic substitution reactions with metals (i.e., "nearest neighbour" and "next-nearest-neighbour" ion displacement interactions [Bleam & Hoffman, 1988] [5], including lead; these reactions result from the positively charged iron-, aluminium-, magnesium- and titanium-based molecules and negatively charged hydroxides, which not only initially adsorb metals but also lead to the long-term "sequestration" phenomenon observed with most inorganic species (Fergusson, 2009) [9]. This feature of MARR differs significantly from the simple ionic binding and precipitation reactions due simply to changes in pH which occur with immobilizing chemicals such as $Ca[OH]_2$ and sodium hydroxide NaOH. The role of both ARR and MARR in removing heavy metals, including cadmium, lead and zinc, from industrial wastewater has been the subject of prior investigation (e.g., Santona et al., 2009), however the application of MARR to highly acidic wastewater is still under review, and its ability to engender micro-concentrations (i.e., concentrations in the parts per billion or µg/L range) of heavy metals in wastewater has not been fully explored. As noted above for ANC, the metal binding capacity (MBC), or "sorption equilibrium point" often denoted as "q", of MARR is approximately 1,000 meq/kg, but this equilibrium point can also be enhanced further with the addition of other additives.

Third, ARR displays flocculating and coagulating properties, and these may inhere to MARR. For example, Wang, et al. (2008) [33] investigated the coagulating and catalysing properties of ARR, and Fu, et al. (2009) [14] examined the relationship between the coagulating properties of ARR, ozonation, reduction in chemical oxygen demand (COD), and the removal of toxic anthraquinone (so-called "disperse blue 56") dye from wastewater. However, research has yet to determine if the intrinsic flocculating and coagulating properties of ARR inhere to MARR, and if so would these benefit the removal of heavy metals from acidic industrial wastewater. These and other relevant phenomena identified with MARR-derived reagents to treat industrial wastewater at sites around the world have been discussed elsewhere (e.g., Fergusson, 2010, pp. 46-61) [10], and applications utilizing these reagents in the treatment of radioactive elements, such as radium, and in industrial and mine site remediation and flue gas scrubbing to sequester mercury, for example, have also been examined (Clark et al., 2011; Fergusson, 2013, 2014; and Hutson & Attwood, 2008) [8, 11, 17] ; other core technical issues associated with the formation of MARR have been the subject of specialist scientific investigations (e.g., Taylor, et al., 2011) [31].

In order to better understand the role of MARR in engendering micro-concentrations of heavy metals in highly acidic industrial wastewater, the present study asked the following research questions: 1) Can the direct addition of chemical reagents derived from modified alumina refinery residue neutralize high levels of acidity to discharge standards and reduce heavy metals, specifically lead, to concentrations of less than 150 micrograms per litre (i.e., 0.15 mg/L, being the discharge consent limit) in highly acidic industrial wastewater; and 2) Can the direct addition of chemicals derived from modified alumina refinery residue reduce the need for flocculants and coagulants when treating heavy metals in highly acidic industrial wastewater? [For the purposes of this study, metal concentrations will be reported in milligrams per litre (mg/L) rather than micrograms per litre (µg/L), but in the context of findings vis-à-vis research question 1) metal concentrations will be discussed in micro-concentrations as µg/L.]

Materials and Methods

Derbyshire has a long history of lead mining. Limestone belts throughout Derbyshire and the Peak District have attracted mining for more than 2,000 years, extending back to at least Roman times and continuing through the Anglo-Saxon, Norman and Victorian eras, with the last mine closing in the 1950s. Geologically, this history can be attributed to lead-rich magma intruded into fissures and faults in the limestone, which when cooled and crystallised left deposits of galena (i.e., lead sulphide, PbS) surrounded by crystals of fluorspar (i.e., calcium fluoride, CaF_2) and calcite (as calcium carbonate, $CaCO_3$). Barium ore has also been found with lead in the region, although some deposits are primarily composed of copper. Lead ore in Derbyshire mostly takes the form of vertical veins several metres across and up to several kilometres in length, with smaller subsidiary veins of lead and other minerals (known locally as "scrins") also filling cavities in the limestone.

The field trial reported in this study was conducted at a lead smelter located in central Derbyshire. The smelter is part of a 4.5 ha site at the center of a 110 ha wooded estate, with part of the site recognized by the UK's Nature Conservancy Council as a "site of special scientific interest". The estate has been naturally forested for hundreds of years, and is home to a large variety of wildlife, including deer. In 1984, the naturally wooded area was supplemented and extended with poplars and a variety of English hardwoods; in the last 20 years, a number of copses have also been planted with tree species selected by ornithologists, providing improved woodland walks for locals and visitors. The smelter, which has a strong track-record of sound environmental stewardship, produces about 75,000 tonnes of lead per year from battery strip production and the recycling of polypropylene components from scrap batteries.

The trial was organized around the removal of three classes of waste. The emphasis of the study was on the first class, namely neutralization of acid (i.e. raising pH, which is chemically simple) and the reduction of lead (II) (i.e., Pb_2^+). Cadmium (II) (Cd_2^+) and zinc(II) (Zn_2^+) were of secondary importance both because of their elevated concentrations and because they had proven difficult to treat in the past; arsenic (As), copper (Cu) and nickel (Ni) were of tertiary concern. While the wastewater generated by lead smelting at the site was highly acidic and contaminated with a variety of metals, based on historical operational evidence the primary focus of this study was on Pb because it was considered the hardest metal for the smelter's wastewater treatment plant (WWTP) to remove in order to meet the stringent consent limits imposed by UK's Environment Agency, the regulatory body governing the site. This study therefore reported all metals, but places a particular emphasis on removal trends and efficiencies for Pb, Cd and Zn.

The WWTP at the site consisted of the following process elements: head of works (i.e., HoW, the inlet of influent from the smelter's processing plant); Tank 1, an equalization tank; Tank 2, a chemical addition tank; Tank 3, a flocculation-

coagulation and settling tank; and discharge point to sewer. Prior to the field trial, the WWTP, which operated on a 24-hour basis, had a maximum flow rate of 1.2 ML per day (or 50 kL/hour) and deployed the following treatment processes: 1) in Tank 1, dose 3.0 g/L of ferric chloride (FeCl$_3$) to aid in flocculation and the settling of solids; 2) in Tank 2, dose trimercapto-s-triazine, trisodium salt (TMT, C$_3$N$_3$S$_3$Na$_3$), a 15% aqueous solution as required (TMT is primarily used to precipitate heavy metals; the chemical characteristics of TMT are not comparable to other triazine compounds, e.g., those used as active ingredients in herbicides); and 3) in Tank 3,

dose 13 mg/L of diallyldimethylammonium chloride (branded as Amerfloc, [(CH$_3$)$_2$N$^+$(CH$_2$CH=CH$_2$)$_2$]Cl$^-$), an industrial polymer used to aid coagulation and settling. It should be noted that none of these three additives chemically "bound" or sequestered Pb or other metals, but simply flocced, coagulated and precipitated them to a solid or semi-solid state, after which they were separated from the liquid stream via filter press, with resultant solids discharged to landfill as a filter cake; wastewater was discharged to the municipal sewerage system after final pH adjustment.

Table 1: Raw pH and metals data of wastewater after Tanks 1 and 2 and field trial parameters.

Sample	Wastewater Parameters				Field Trial Parameters			
	pH	Pb (mg/L)	Cd (mg/L)	Zn (mg/L)	ElectroBind Type (A/B)	FeCl$_3$ (on/off)	TMT (on/off)	Amerfloc (on/off)
1	2.3	4.0	14.2	58.7	A	on	on	on
2	2.3	4.6	27.9	105.9	A	on	on	on
3	—	3.9	42.7	55.6	A	on	on	on
4	—	7.3	26.3	79.1	A	on	on	on
5	2.4	3.3	3.8	26.1	A	on	off	off
6	2.3	7.1	4.1	82.3	A	on	off	off
7	2.3	3.8	5.6	42.6	A	on	off	off
8	2.4	3.1	7.1	36.0	A	on	off	off
9	2.4	3.9	5.3	37.9	A	on	off	off
10	2.3	3.4	5.9	73.8	A	on	off	off
11	2.2	3.4	4.2	32.6	A	on	off	off
12	1.4	5.1	4.2	39.0	A	on	off	off
13	1.3	5.0	5.0	115.8	A	off	off	off
14	1.2	2.8	1.4	11.1	A	off	off	off
15	1.3	3.8	2.3	34.7	A	off	off	off
16	—	2.9	2.3	63.7	A	off	off	off
17	—	4.5	0.6	8.6	A	off	off	off
18	—	4.7	1.4	21.0	A	off	off	off
19	1.2	3.8	1.6	21.1	A	off	off	off
Average After Tank 1	1.7	4.2	8.7	49.8	—	—	—	—
20	1.3	3.0	5.8	53.1	B	off	off	off
21	1.4	3.2	5.6	71.9	B	off	off	off
22	—	4.0	2.7	25.4	B	off	off	off
23	1.3	3.2	2.9	17.3	B	off	off	off
24	1.3	3.1	2.4	15.4	B	off	off	off
25	1.3	3.1	0.5	6.7	B	off	off	off
Average After Tank 2	1.3	3.3	3.3	31.6	—	—	—	—

As shown in Table 1, the average profile of influent to the site's WWTP during the trial pH averaged 1.7 after Tank 1 and 1.3 after Tank 2, Pb averaged 4.2 mg/L after Tank 1 and 3.3 mg/L after Tank 2, Cd averaged 8.7 mg/L after Tank 1 and 3.3 mg/L after Tank 2, and Zn averaged 49.8 mg/L after Tank 1 and 31.6 mg/L after Tank 2. While pH was sampled and measured after Tank 1, it should not be concluded that the average pH of 1.7 was due to the addition of FeCl$_3$, which has a pH of 2.0.

As shown in Table 1, FeCl$_3$ was discontinued during the trial after day 12, but the pH in Tank 1 continued to average 1.25 between days 13 and 19. Not shown in Table 1 is the average influent data after Tank 1 for As 0.17 mg/L, Cu 1.4 mg/L and Ni 6.1 mg/L, as these metals were not monitored on a daily basis during the field trial, with only ten sampling points throughout the trial. The consent limits for the discharge of treated wastewater from the site were: pH 6.0-10.0; Pb 0.15 mg/L; Cd 0.15 mg/L; Zn 0.3 mg/L; As 0.5 mg/L; Cu 0.5 mg/L; and Ni 0.5 mg/L. From this data it can be seen that all analytes, except As, were outside consent limits prior to treatment.

The 25-day field trial consisted of the on-site direct addition of a MARR-derived chemical reagent called Electro Bind,

supplied by Australian environmental company Virotec, to an average 950 kL/day (or 40 kL/hour) of industrial process water. Two different blends of ElectroBind additive were used in this trial: Electro Bind A, which contained magnesium-enhanced MARR, the magnesium oxide (MgO) being added for greater ANC (as noted above, the ANC of MARR is approximately 3.6 mmoles of acid/kg, but the added MgO increased this to approximately 19.0 mmoles of acid per kg); and Electro Bind B, which was almost entirely composed of just MARR.

Electro Bind A was added directly to the liquid stream, i.e., the solvent, at a rate of 0.25 g/L in Tank 1 after the HoW where pH averaged 1.7, and Electro Bind B was added to the liquid stream at a rate of 0.25 g/L in Tank 2, where pH of wastewater prior to the trial averaged 1.3. The required dose rates was determined in pre-trial laboratory experiments. In this trial therefore, the total 0.5 g/L of Electro Bind reagents A and B, which was added as a 5% slurry to the liquid stream, acted as the sorbent and heavy metals acted as the sorbate. During the 25-day field trial, 19 samples were collected immediately after Tank 1 (days 1-19) and six samples were collected immediately after Tank 2 (days 20-25). Inlet and treated samples were filtered using a 0.2 μm Microstart

syringe filter, and an in-line automated volumetric system was used for metals analysis during the trial, with replicate samples re-tested using inductively coupled plasma mass spectrometry (ICP-MS) after the trial; pH readings were taken during the trial using a Schott bench meter.

Previous data have shown that in addition to pH, factors which affect the removal of Pb and other heavy metals from wastewater include dose rate of sorbent and contact time between sorbent and sorbate. In this field trial, the contact time of ElectroBind A in Tank 1 was approximately 30 minutes and contact time of ElectroBind A and B in Tank 2 was approximately 30 minutes, for a total contact time between sorbent and sorbate in the entire treatment process from HoW to final discharge being approximately two hours.

Results and Discussion

For the purposes of this trial, pH and concentrations of metals after Tank 2 were assumed to be the same as those at the discharge point, which is reasonable given that no further treatment of effluent occurred in the WWTP during the field trial after Tank 2. It should also be noted that between days 5 and 25, Amerfloc addition to Tank 3 was discontinued, and therefore no chemical addition occurred in Tank 3 or beyond during this trial beyond day 4.

Table 2 presents the raw data for pH and metal removal concentrations and efficiencies over the course of the 25-day

field trial. Table 2 shows that the average pH after ElectroBind A addition in Tank 1 was 9.3, and after ElectroBind B addition in Tank 2 was 9.5, both within consent limits.

Concentrations of Pb averaged 0.14 mg/L after Tank 1 and 0.11 mg/L after Tank 2, with removal efficiencies averaging 96% in both cases; Cd averaged 0.11 mg/L after Tank 1 and 0.05 mg/L after Tank 2, with removal efficiencies averaging 98% in both cases; and concentrations of Zn averaged 0.09 mg/L after Tank 1 and 0.05 mg/L after Tank 2, with removal efficiencies averaging 99% in both cases. Research question #1 was therefore answered in the affirmative, with pH between 6.0-10.0, Pb at 110 µg/L (or 110 parts per billion), Cd at 50 µg/L (or 50 parts per billion), Zn at 50 µg/L (or 70 parts per billion), As at 0.7 µg/L (or 0.7 parts per billion), Cu at 6.0 µg/L (or 6.0 parts per billion), and Ni at 20 µg/L (or 20 parts per billion); average pH and micro-concentrations of all heavy metals were below consent levels after treatment. Not presented in Table 2 are average results for As, Cu, and Ni, which indicated As was reduced from 0.17 mg/L to 0.0007 mg/L, a 99% removal efficiency; Cu was reduced from 1.4 mg/L to 0.006 mg/L, a 99% removal efficiency, and Ni was reduced from 6.1 mg/L to 0.02 mg/L, a 99% removal efficiency. Average post-treatment concentrations of As, Cu and Ni were below consent levels.

Table 2: Raw pH and metals data after treatment with ElectroBind A and B during the 25-day field trial.

Sample	pH	Pb (mg/L)	Removal Efficiency (%)	Cd (mg/L)	Removal Efficiency (%)	Zn (mg/L)	Removal Efficiency (%)
1	9.3	0.04	99	0.21	98	0.07	99
2	9.3	0.15	97	0.33	98	0.11	99
3	—	0.11	97	0.38	99	0.16	99
4	—	0.11	98	0.47	99	0.17	99
5	9.4	0.16	95	0.17	98	0.09	99
6	9.4	0.23	97	0.07	98	0.06	99
7	9.3	0.02	99	0.01	99	0.04	99
8	9.3	0.35	89	0.11	98	0.03	99
9	9.3	0.27	93	0.15	97	0.17	99
10	9.4	0.60	83	0.02	99	0.15	99
11	9.3	0.33	90	0.02	99	0.16	99
12	9.3	0.03	99	0.06	99	0.08	99
13	9.4	<0.01[†]	100	0.02	99	0.05	99
14	9.3	0.1	98	0.04	99	0.07	99
15	9.2	0.05	98	0.07	95	0.11	99
16	—	0.16	96	0.02	99	0.09	99
17	—	<0.01[†]	100	0.02	99	0.07	99
18	—	<0.01[†]	100	0.02	95	0.07	99
19	9.3	<0.01[†]	100	0.02	99	0.09	99
Average After Tank 1	9.3	0.14	96	0.11	98	0.09	99
20	9.4	0.12	96	0.16	93	0.06	99
21	9.6	0.23	93	0.08	99	0.06	99
22	9.3	0.04	99	0.01	99	0.04	99
23	9.5	0.13	96	0.03	99	0.04	99
24	9.5	0.11	96	0.02	99	0.04	99
25	9.5	0.08	97	0.03	99	0.07	99
Average After Tank 2	9.5	0.11	96	0.05	98	0.05	99

[†] Below the limit of detection

The discontinuation of FeCl₃ on day 13, and the discontinuation of both TMT and Amerfloc on day 5 apparently made no difference to these results, meaning that ElectroBind reagents A and B single-handedly replaced the functions of flocculation, precipitation and coagulation provided by FeCl₃, TMT and Amerfloc, thus answering research question #2 in the affirmative.

Figure 1 shows the trend analysis for Pb concentrations over the 25-day trial period. The four main Pb spikes in influent on day 4 (7.3 mg/L), day 6 (7.1 mg/L), days 12-13 (5.1 mg/L and 5.0 mg/L) and days 17-18 (4.5 mg/L and 4.7 mg/L) cannot obviously be seen as spikes in post-treatment Pb concentrations. The general flattening of Pb spikes after days 10-12 was viewed favorably by the smelter's WWTP operators, signaling in their minds that the management of Pb

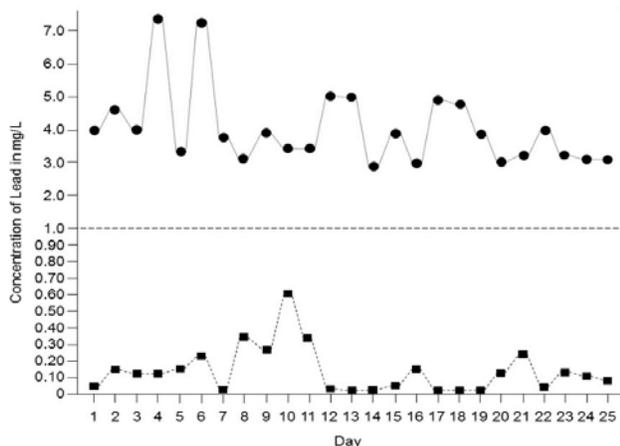was under control as a result of the changes in reagent addition types.

Fig 1: 25-day trend analysis of influent (top) and effluent (bottom) for lead concentrations in mg/L.

Figure 2 presents the trend analysis over 25 days for the removal of Cd, including the observation that Cd was stably low after day 5. Of note is the way post-treatment concentrations of Cd almost exactly correlate with pre-treatment concentrations in Tank 1 influent. For example, at day 3, influent Cd concentrations reached their highest point at 42.7 mg/L and on days 3 and 4, post-treatment Cd concentrations in Tank 1 reached their apogee at 0.38 mg/L and 0.47 mg/L respectively. Similarly, the two smaller spikes in untreated Cd on day 8 (7.1 mg/L) and again on days 20 (5.8 mg/L) and 21 (5.6 mg/L), are reflected in spikes of 0.15 mg/L on day 9, 0.16 mg/L on day 20, and 0.08 mg/L on day 21. This overall downward trend had not been previously observed by WWTP operators with the addition of other additives, thus making sustainable management of Zn in the smelter's wastewater both unpredictable and difficult to manage in the past.
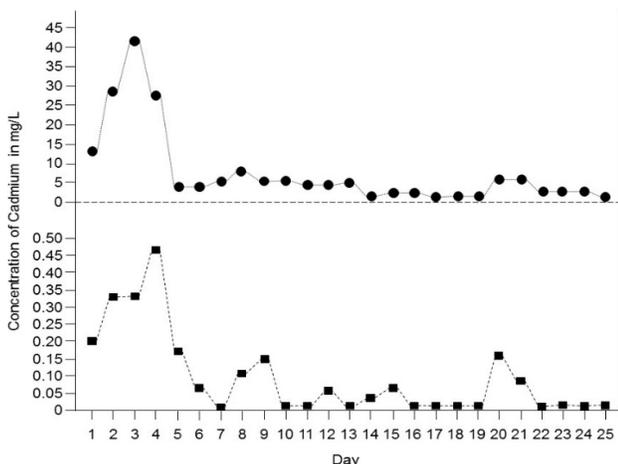

Fig 2: 25-day trend analysis of influent (top) and effluent (bottom) for cadmium concentrations in mg/L.

As shown in Figure 3, Zn concentrations varied wildly in the influent (ranging from a low of 6.7 mg/L on day 25 to a high of 115.8 mg/L on day 13) but after treatment did not show the same spike trends as Cd and Pb. Allowing for the same initial acculturation period of 5-7 days for pH, Pb and Cd, relatively large spikes in Zn occurred at days 9-11, day 15 and day 19.

While an overall downward trend can be observed (with average Zn concentrations in the first half of the trial between days 1-11 of 0.11 mg/L being significantly higher than those in the second half of the trial between days 12-25 at 0.06 mg/L, albeit in relatively narrow bands of 0.14 mg/L to 0.07 mg/L respectively) and discharge consent limits were reached, these data do not show stability in Zn concentrations in treated effluent during the trial.
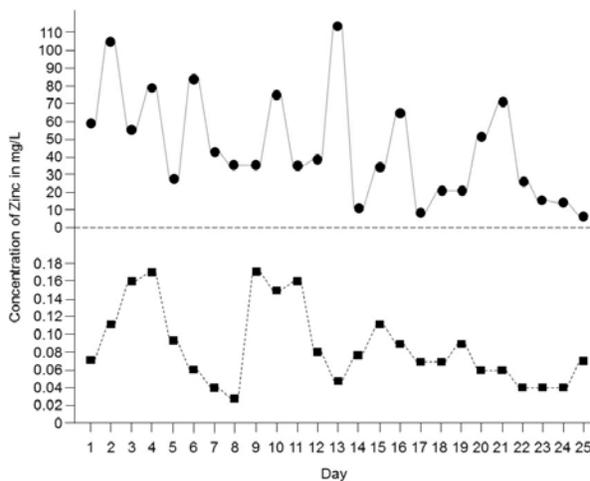

Fig 3: 25-day trend analysis of influent (top) and effluent (bottom) for zinc concentrations in mg/L.

A comparable analysis of the relationship between pH and metals was not relevant, as pre-treatment pH from days 1-11 (average of 2.3, within a range of 0.2 units), pre-treatment pH from days 12-25 (average of 1.3, within a range of 0.2 units), and post-treatment pH from days 1-25 (average of 9.4, within a range of 0.4 units) were uniform enough within these time periods to disallow comparison to the fluctuating changes in both pre- and post-treatment metal concentrations during the same periods; in other words, influent and effluent pH was uncorrelated to metal concentrations due to the uniformity of pre- and post-treatment pH during the course of the field trial.

This trial verified that the addition of chemical reagents derived from modified alumina refinery residue can neutralize extremely high levels of acidity and decrease heavy metals, specifically lead(II), in industrial wastewater to micro-concentrations of less than 150 parts per billion. The trial simultaneously showed that these reagents replace the need for standard industrial flocculants and coagulants.

However, further research is required to optimize the chemical interventions considered by this study and to better understand the chemical reactions reported herein. For example, a mass balance of heavy metals, particularly of lead (II), would provide the necessary data required to determine the sorption equilibrium point (q) of Electro Bind reagents A and B. While this has been carried out under different industrial conditions, the projected q of >1,000 meq/kg used for this study is an estimate based on earlier data, and therefore requires further investigation. The question of whether both sorbents contributed equally or unequally to sorption equilibrium remains unanswered.

Similarly, the optimisation of Electro Bind blends (i.e., more or less magnesium addition) would allow for a more detailed calibration of solvent: sorbate ratios, particularly under differing flow rates and pH conditions, and a more detailed calibration of dosing rates of Electro Bind in Tanks 1 and 2 would have provided valuable data on the specific chemical

reactions which caused the floccing, coagulation and precipitation phenomena observed in this field trial. The precise relationship between various levels of acidity, dosing rates, flow rates, Electro Bind blends, heavy metal concentrations, ionic binding mechanisms, and flocking and coagulating should be the subject of further controlled investigation.

Moreover, there is little research data in the literature to explain the floccing and coagulating phenomena of modified alumina refinery residue observed in this study. For example, it is by no means clear what mechanisms are in play or exactly what dosing rates of MARR, chemical reactions, pH or other factors are relevant in the context of floccing and coagulating industrial wastewater. Certainly the fine-grained powder of MARR (80% of which is <10 micron) with its positively and negatively charged molecules may play a part in this phenomenon, but other chemical and physical properties of the material, including the relationship between potential counter-ionic effects and coagulation performance and the relationship between rate and intensity of mixing with settling of solids, need to be examined.

Clearly MARR does not obviously share the same electrolytic or poly-electrolytic characteristics of standard polymers, such as ionic and cationic polyacrylamides, but what in its chemistry could account for the floccing and coagulating outcomes reported here? While the work of Wang, et al. (2008) [33] and Fu, et al. (2009) [14] approaches these issues, it generally fails to answer fundamental research questions about floccing and coagulation, preferring instead to focus more on the oxidation, hydrogenation and hydrodechlorination effects of MARR in relation to wastewater treatment.

Using both boric acid and phosphomolybdic acid (i.e., inorganic modification) as well as oligomers of aniline formaldehyde (i.e., organic modification) to convert ARR into MARR, Bhat, et al. (2011) [3] examined the role of MARR as a nanofiller in a polymeric matrix and investigated the chemical bonding and "strong interaction" at the nanofiller-matrix interface. Bhat's research, while not directly related to industrial wastewater and the floccing and coagulating properties of MARR, did study the physical topography of the composite materials after addition to vinyl alcohol, and showed that MARR is more thermally stable than polymers alone, which was attributed to the presence of silicates in MARR.

This research was subsequently expanded by Bhat, et al. (2012) [4], and provides preliminary evidence as to why it is worth pursuing a more comprehensive understanding of the relationship between MARR and its polymeric characteristics. These characteristics may be due largely to the presence of heavier silicates, but more work needs to be carried out to examine the relationship between silicates and other compounds in MARR, such iron and aluminium both of which may have polymeric properties under certain conditions, and the floccing and coagulating properties of MARR in industrial wastewater.

A more precise calculation of the ANC of MARR would also be useful beyond the approximation of 19.0 mmoles of acid/kg reported here. Expanding the investigatory parameters of further research to include data on the amenability of sequestration of all metal and metalloid types and other contaminants into the solid matrix of MARR, and the adsorption of phosphate, nitrogen and cyanide, by way of obvious examples, would further our understanding of the scope and potential of modified alumina refinery residue to provide a chemically and financially viable alternative to the more commonly applied chemical agents in wastewater treatment. Nevertheless, the findings reported in this study go some of the way to answer basic questions about the role modified alumina refinery residue might play in the removal of heavy metals, particularly lead, from highly acidic industrial wastewater.

References
1. Agency for Toxic Substances and Disease Registry. Toxicological profile for lead. Atlanta, Georgia: U.S. Department of Health and Human Services, Public Health Service, 1999.
2. Bellinger DC. Lead neurotoxicity in children: Decomposing the variability in dose-effect relationships. Amer. J Ind Med. 2007; 50:270-278.
3. Bhat AH, Abdul Khalil HPS, Banthia AK. Thermoplastic polymer based modified red mud composites materials. In B. Attaf (ed.), Advances in Composite Materials—Ecodesign and Analysis Rijeka, Croatia: In Tech. 2011, 55-86.
4. Bhat AH, Khalil HPSA, ul Huq Bhat U, Banthia AK. Dielectric and material properties of poly (vinyl alcohol): Based modified red mud polymer nanocomposites. J Pol Envir. 2012; 20:395-403.
5. Bleam WF, Hoffman R. Isomorphous substitution in phyllosilicates as an electronegativity perturbation: Its effect on bonding and charge distribution. Inorg Chem. 1988; 27:180-3186.
6. Brashear CW, Kopp VJ, Krigman MR. Effect of lead on the developing peripheral nervous system. J Neuropath. Exper Neurol. 1978; 37:414-425.
7. Campbell JR, Auinger P. The association between blood lead levels and osteoporosis among adults—Results from the Third National Health and Nutrition Examination Survey (NHANES III). Envir. Health Persp 2007; 115:1018-1022.
8. Clark MW, Akhurst D, Fergusson L. Removal of radium from groundwater using a modified bauxite refinery residue. J Envir. Qual. 2011; 40:1835-1843.
9. Fergusson L. Commercialisation of environmental technologies derived from alumina refinery residues: A ten-year case history of Virotec, Commonwealth Scientific and Industrial Research Organisation (CSIRO), Project ATF-06-3 "Management of Bauxite Residues", Department of Resources, Energy and Tourism (DRET), Commonwealth Government of Australia, representing part of the commitment of the Australian Government towards the Asia-Pacific Partnership on Clean Development and Climate, November, 2009.
10. Fergusson L. Virotec: A ten-year story of success in environmental remediation. Gold Coast, Australia: Prana World Publishing, 2010.
11. Fergusson L. An industrial legacy now gone. Water Man. Envir. 2013; 24:40.
12. Fergusson L. Beneficial reuse: A field trial to remediate and a bench-scale test to revegetate coal seam gas dam

sediments from Queensland. Am. J Envir Prot. 2014; 3:249-257.

13. Fischbein A. Occupational and environmental lead exposure. Rom, W.N., editor. In: Environmental and Occupational Medicine, 3rd Edition. Philadelphia: Lippincott-Raven, 1992, 973-976.

14. Fu J, Ding Y-H, Ma G-Y, Yang J, Zeng Q-F, Liu, M-Y *et al.* Removal of a toxic anthraquinone dye by combination of red mud coagulation and ozonation. Ozone Science Eng 2009; 31:294-300.

15. Habashi F. Bayer process for alumina production: Historical perspective. Bull. Hist. Chem. 1995; 17/18:15-19.

16. Ho Y-S. Effect of pH on lead removal from water using tree fern as the sorbent. Bio. Tech 2005; 96:1292-1296.

17. Hutson NS Attwood .C. Binding of vapour-phase mercury (Hg0) on chemically treated bauxite residues (red mud). Envir. Chem. 2008; 5: 281-288.

18. Gartley K. Soil test notes: Note 17 managing lead contaminated soils. Newark, Delaware: University of Delaware, Soil Testing Laboratory. 2002.

19. Katsou E, Malamis S, Haralambous K. Pre-treatment of industrial wastewater polluted with lead using adsorbents and ultrafiltration or microfiltration membranes. Wat. Envir. Res 2011; 83:298-312.

20. Khaoya S, Pancharoen U. Removal of lead (II) from battery industry wastewater by HFSLM. Int. J Chem Eng. App 2012; 3:98-103.

21. Lustberg M, Silbergeld E. Blood lead levels and mortality. Arch Int Med 2002; 162:2443-2449.

22. Mengistie AA, Rao TS, Rao AVP, Singanan M. Removal of lead (II) ions from aqueous solutions using activated carbon from Militia Ferruginea plant leaves. Bull. Chem. Soc. Ethiopia 2008; 22:349-360.

23. National Health and Medical Research Council. Review of lead exposure and health effects in Australia. National Health and Medical Research Council, Federal Government of Australia, NHMRC reference no. EH55. Canberra, Australia, 2014.

24. National Research Council. Measuring lead exposure in infants, children and other sensitive populations. Washington, D.C.: National Academy Press, 1993.

25. Needleman HL, Riess JA, Tobin M, Biesecker G, Greenhouse JB. Bone lead levels and delinquent behavior. J Amer Med Assoc. 1996; 275:363-369.

26. Rao SM, Raju GC. Comparison of alkaline treatment of lead contaminated wastewater using lime and sodium hydroxide. J. Water Res. Prot. 2010; 2:282-290.

27. Rubinos D, Díaz-Fierros F, Barral MT. Neutralization and decontamination of acid leachates using bauxite red mud. Rüde TR, Freund A, Wolkersdorfer C, editors. In: 11th International Mine Water Association Congress – Mine Water – Managing the Challenges. Aachen, Germany: International Mine Water Association. 2011, 441-446.

28. Santona L, Castaldi P, Melis P. Evaluation of the interaction mechanisms between red muds and heavy metals. J Haz Mat 2006; 136:324-329.

29. Singanan M. Removal of lead (II) and cadmium (II) ions from wastewater using activated carbon. Science Asia. 2011; 37:115-119.

30. Taylor MP. Lead poisoning of Port Pirie children: A long history of looking the other way. The Conversation. July 19, 2012.

31. Taylor K, Mullett M, Adamson H, Wehrli J, Fergusson L. Application of nanofiltration technology to improve sea water neutralization of Bayer process residue. In S.J. Lindsay (ed.), Light Metals 2011 Hoboken, New York: John Wiley & Sons, 2011, 79-87.

32. Teekayuttasakul P, Annachhatre AP. Lead removal and toxicity reduction from industrial wastewater through biological sulfate reduction process. Journal of Environmental Science and Health, Part A, Toxic/Hazardous Substances & Environmental Engineering. 2008; 43:1424-30.

33. Wang S, Ang HM, Táde MO. Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes. Chemosphere. 2008; 72:1621-1635.

34. World Health Organization. Childhood lead poisoning. Geneva, Switzerland: WHO Press, 2012.