REMOVING INORGANIC CONTAMINANTS FROM HUMAN DRINKING WATER USING MODIFIED RED MUD

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Abstract

At previous Alumina Quality Workshops, we have shown that red mud can be chemically and physically treated to form Bauxsol™ materials, which have a near-neutral pH, a good acid neutralisation capacity, an excellent metal binding capacity and a very high reactive surface area. In this paper we show how further chemical treatment and pelletisation can produce materials that can remove several hazardous contaminants from drinking water. The pellets meet NSF standards for direct contact with drinking water and are currently being used in several water treatment plants. One pelletised reagent (Radium ProActive™) is being used to lower radium concentrations in potable water from well above the regulatory limit of 5 pg/L to < 0.5 pg/L. These pellets also remove common trace metals (e.g. copper, zinc and cadmium), some less common elements (e.g. uranium), and lower gross alpha counts for the water to well below regulatory limits. If the Bauxsol™ reagent is acid treated then water washed before pelletisation, the pellets can be used to lower arsenic concentrations in water to < 1 µg/L. However, the arsenic must be present in the more oxidised arsenate form (arsenite can be converted to arsenate using an oxidant such as during chlorination) and the pH of the water should be kept below 6.5 for optimum performance and above 6.0 to meet regulatory limits. In this paper we describe the preparation of these new materials and present data for several water treatment applications in North America.

Introduction

At the 6th International Alumina Quality Workshop in Brisbane, a simple procedure was described (McConchie *et al.* 2002) whereby the soluble basicity in caustic red mud residues from alumina refineries could be converted to solid alkalinity in such a way that the acid neutralising capacity of the material was preserved but the pH was lowered to about 8.5 (see also McConchie *et al.* 1999, 2000, Hanahan *et al.* 2004, Menzies *et al.* 2004). The procedure uses inexpensive and readily available materials such as seawater, hard groundwater brines, or industrial wastewater brines with a high Mg and Ca content (e.g. bittern brines from salt works); Mg and Ca can also be added as the chloride salts to reduce the required fluid volumes. The solid material resulting from the treatment (referred to as Bauxsol™) easily passes the TCLP test for classification as an inert solid (McConchie *et al.* 2002), is non-toxic and environmentally benign (e.g. Brunori *et al.* 2005, Maddocks *et al.* 2005), has a good acid neutralising capacity and an excellent trace metal binding capacity (e.g. McConchie *et al.* 1999, 2000, 2002, 2003).

Bauxsol™ can be used in a wide range of environmental remediation and industrial applications (e.g. Lin *et al.* 2002, Davies-McConchie *et al.* 2002, McConchie *et al.* 2002, 2003, Maddocks *et al.* 2004, Clark *et al.* 2004, 2006, Munro *et al.* 2004, Lapointe *et al.* 2005, 2006, Akhurst *et al.* 2006, Fytas 2007) where its natural buffering capacity means that dose rates do not need to be carefully controlled and it provides greater long term stability than conventional lime-based treatments (e.g. McConchie *et al.* 2003, Paradis *et al.* 2007). Bauxsol™-based products are now being used in several countries to treat contaminated water and soil and excellent results are being achieved. Some applications were outlined at the 7th International Alumina Quality Workshop in Perth (McConchie *et al.* 2005) and include the treatment of solid and liquid wastes associated with mining and mineral processing activities, electroplating plants, tanneries and CCA wood treatment plants, and improving effluent quality from sewage treatment plants, intensive farming operations and composting operations. Procedures have also been developed to pelletise the Bauxsol™ material (Clark *et al.* 2005) so that it can be used to treat flowing water and the pellets are being used successfully in several water treatment applications.

With the ability to treat flowing water and to lower the concentrations of many hazardous elements to well below drinking water standards, there is obvious potential for using pelletised Bauxsol™ to treat human drinking water. In particular, there is excellent potential for removing highly hazardous contaminants such as arsenic, radium, uranium and gross alphas to well below acceptable limits and for doing this using simple and inexpensive equipment that can easily be installed and maintained in developing world countries and remote areas elsewhere; the concentrations of other metals, fluoride and phosphate are also greatly reduced.

Arsenic concentrations are low in most natural waters (< 5 µg/L; mean oceanic concentration is 3.7 µg/L), but there are many parts of the world where dissolved arsenic concentrations in groundwater are much higher as a result of natural geochemical processes or, less commonly, as a result of human activity. Natural processes mainly involve hydrothermal exhalations (e.g. Pope *et al.*, 2004), oxidative decomposition of sulphide minerals with a high arsenic content (particularly arsenopyrite), and the development of reducing conditions that favour the conversion of arsenate ($As^{(V)}$), which may be bound to iron oxyhydroxides or similar minerals (e.g. Ahmed *et al.*, 2004), to much more mobile arsenite ($As^{(III)}$); the conversion of $As^{(V)}$ to $As^{(III)}$ can be greatly enhanced by micro-organisms. Human activity can affect arsenic concentrations directly through industrial pollution (either planned discharges or accidental spillages) or indirectly when drainage work or the use of groundwater resources alters the position of the water table in such a way that consequential changes in geochemical conditions in the aquifer allow the mobilization of previously immobile arsenic. Whatever the exact reason for high dissolved arsenic concentrations in particular groundwaters, its presence can restrict or preclude use of the water for human consumption because there is no known cure for arsenic poisoning. Arsenic concentrations that exceed the accepted safe limit of 10 µg/L can be found in groundwater in many countries

throughout the world (e.g. Genç 2003, Genç-Fuhrman *et al.* 2004a,d) but the worst affected area is the Bengal delta area of Bangladesh and India where arsenic concentrations can be particularly high (>200 µg/L) and large populations depend on groundwater as a drinking water resource. It has been estimated (Chowdhury *et al.*, 2000) that as many as 80 million people in Bangladesh and 40 million people in India consume groundwater with a sufficiently high arsenic content that they risk arsenic poisoning. Natural arsenic contamination of potentially potable groundwater is also a problem in highly developed countries and U.S. government estimates suggest that arsenic concentrations are over the regulatory limits for human consumption in water from at least 40% of all wells west of the Mississippi River.

The world average Ra concentration in seawater is only 0.089 pg/L (9×10^{-7} mg/kg) but in some groundwaters that come into contact with rocks (mainly granites, gneisses, shales and some phosphatic strata) with elevated concentrations of the parent elements, U and Th, groundwater Ra concentrations can exceed 10 pg/L. The sixteen isotopes of Ra form by radioactive decay of other elements but only two have half lives longer than a few days; ^{226}Ra has a half life of about 1,600 years before decaying through a series of nine (mostly short-lived) daughter isotopes to ^{206}Pb; ^{228}Ra has a half life of about 5.75 years before decaying through a series of nine (mostly short-lived) daughter isotopes to ^{208}Pb. Each step in both decay series involves the emission of either α or β particles together with X-rays and γ-rays. Although radium is a daughter product of uranium and thorium decay, disequilibrium in the proportions of parent and daughter isotopes often exists as a result of differential dispersion of particular elements under the prevailing geochemical conditions in the groundwater aquifer. Hence, high Ra concentrations can occur, with or without contributions from other radioisotopes (particularly radon gas and often uranium), but will usually mean that the water will also have a gross alpha particle activity that is above acceptable limits (15 pCi/L in the U.S.A.). Radium is seldom present at elevated concentrations in groundwater to be used for human consumption, but where it is present, it is hazardous because all its isotopes are radioactive and because it can be readily taken up by the human body. Radium is chemically similar to calcium and it can substitute for Ca in the body and accumulate in bones where α radiation can damage tissue and ultimately lead to bone cancer. Because Ra is highly hazardous, most countries have adopted a limit of 5 pg/L for the activity of ^{226}Ra + ^{228}Ra in drinking water (1 pg of Ra has an activity of 1 pCi or 0.037 Bq). Total radium concentrations (^{226}Ra + ^{228}Ra) and gross alpha particle activity are over the regulatory limits for human consumption in many wells in the U.S.A. (e.g. 43 community water systems are out of compliance in the State of Colorado alone; CO-RADS, 2007) and unacceptable radium concentrations (i.e. > 5 pCi/L) undoubtedly also exist in many countries where comprehensive analyses have not been carried out (Vengosh 2006). Vengosh (2006) also noted that some highly mineralised bottled waters have a radium concentration of 78 pCi/L, which is about fifteen times the maximum allowed in drinking water in the U.S. Naturally elevated uranium concentrations are often, but not always, over acceptable limits (i.e. > 30 µg/L) in the same wells that are out of compliance with respect to radium.

Removal of radium from drinking water

After good results were obtained in laboratory studies and large-scale field trials, certification was obtained from NSF International to allow the use of Bauxsol™-based materials to treat human drinking water. The Bauxsol™-based materials easily met the NSF standards for human drinking water treatment, but there were several problems with optimising treatment procedures that had to be overcome. The main problems, how they were overcome and the results that can be obtained using Bauxsol™-based materials to treat drinking water are outlined below.

The first trials using water treatment by flow through a single column (10 cm diameter PVC column c. 1.2 m long) containing about 8 kg of pelletised Bauxsol™ reagent (marketed as Radium ProActiv™) provided the results shown in Table 1.

Table 1. Result of treating drinking water from a South Carolina well to remove radium

Analyte	Before (pCi/L)	After (pCi/L)
^{226}Ra	2.01 ± 0.18	0.11 ± 0.05
^{228}Ra	7.98 ± 0.93	0.47 ± 0.50
^{226}Ra + ^{228}Ra	9.99 ± 1.11	0.58 ± 0.55

NOTE: For radium, an activity of 1 pCi/L is equal to a Ra concentration of 1 pg/L and an activity of 0.037 Bq/L. The U.S. regulatory limit for human drinking water is 5 pCi/L.

In this trial about 12.5 L of water were treated for each gram of Bauxsol™ reagent present resulting in a radium loading on the material of 118 pCi/g. However, the trial was terminated at this point, so that leaching tests could be carried out on the reagent in the column, although there was no evidence for any substantial decrease in radium removal efficiency. When the Bauxsol™ removed from the column was subjected to the standard TCLP leaching test, the total Ra concentration in the extracting fluid was 0.4 pCi/L and well below allowable limit of 150 pCi/L for ^{226}Ra and ^{228}Ra. Hence, the spent Bauxsol™ reagent would be classed as an inert solid and could be safely disposed of in a municipal landfill provided that the total radium content of the spent reagent also remained below State regulatory limits. A cost-benefit analysis showed that although the Bauxsol™ reagent could remove much more Ra before its Ra removal efficiency decreased significantly, it would be better to limit the amount of water treated per unit mass of reagent so that the total activity of the spent reagent remained below regulatory limits and it could be disposed of in a municipal landfill. If treating more water raised the total activity of the spent reagent above the regulatory limits, the spent reagent would have to be disposed of in a radioactive waste repository at considerable cost. Hence, the volume of water that can be treated per unit mass of Bauxsol™ reagent is determined by the total activity of the spent reagent and not by whether there has been any decrease in the ability of the reagent to remove more Ra.

Although the high efficiency of Ra removal by the Bauxsol™ reagent makes it very effective for treating drinking water, it also causes a problem because it means that after treating a large volume of water, reagent at the input end of the column has a much higher total activity than reagent at the output end and the maximum activity allowed by the regulations applies to the most active part of any system. Therefore, to spread the activity more widely, it would be better to have short columns with a large diameter but then the flow path length in the column would be too short for efficient contaminant removal. One solution to this problem is to use tall columns with large diameters and to inject the water into the columns at multiple points between the input and the output ends to spread the activity within the column. Trials using this procedure show that it works well. The alternative approach is to use four (or more) short large diameter columns in a counter current flow arrangement. In the counter current flow arrangement the columns are linked in series and the water flows through each column in turn, meaning that column 1 at the input end will reach its allowable activity limit first. At this point, column 1 would be removed, emptied and recharged with new reagent, column 2 would become the new first column in the series and the recharged column would be added back into the series as a new last column, and so on. A water treatment trial, for a well in Missouri, using four columns in a counter current flow arrangement showed that it is effective and simple to operate. This trial used four columns (10 cm diameter and 120 cm long) each containing 5 kg of Radium

ProActiv™ pellets with a size range from 6 mm to 10 mm and 1.2 kg of washed river gravel that was placed above and below the pellets to inhibit preferential flow path development; the porous pellets have a bulk density of 0.743 kg/L and a porosity of about 66%). Aquifer water was fed through the columns at a rate of 1 gallon per minute 24 hours per day for 12 weeks to give a total volume of treated water of 31,958 gallons and a residence time in the columns of 6.28 minutes. In this trial the mean gross alpha activity was lowered from 25.8 pCi/L to below the regulatory limit of 15 pCi/L for 54 days and the combined $^{226}Ra + ^{228}Ra$ was lowered from 17.84 pCi/L to below the regulatory limit of 5 pCi/L for 40 days; however, even after 84 days (457,883 L treated) the columns were still removing 24.3 % of the gross alphas and 39.7% of the combined $^{226}Ra + ^{228}Ra$ in the influent water. These results indicate that the treatment of water with an initial mean gross alpha activity of 25.8 pCi/L and a combined $^{226}Ra + ^{228}Ra$ of 17.84 pCi/L to drinking water standards required less than 0.1 g of treatment reagent per litre of water treated. Furthermore, because the ability of the Radium ProActiv™ pellets was not exhausted at breakthrough, it is highly likely that increasing the residence time could further increase contaminant removal efficiencies. However, there is little merit in further increasing the contaminant removal efficiency because the maximum total activity of the spent pellets that would allow disposal in ordinary municipal landfill would have been exceeded. It was also noted during the Missouri trial that as a result of passing through the columns, the pH increased slightly from 7.02 to 7.30 while the copper concentration decreased from 0.010mg/L to ≤ 0.002mg/L, the iron concentration decreased from 0.055mg/L to ≤ 0.01mg/L, the lead concentration decreased from 0.007mg/L to ≤ 0.002mg/L, and the zinc concentration decreased from 0.042mg/L to 0.017mg/L.

Large-scale trials also revealed the problem that when new columns were first used, well over 500 empty bed volumes of water had to be flushed through the columns to lower the pH of the treated water to < 8.0. When the first water was flushed through the column the pH could be over 11.0 because the pelletised reagent was bound with Ordinary Portland Cement (OPC, see Clark *et al.* 2005) that caused a significant rise in water pH until equilibration was achieved. Furthermore, if flow through the columns was shut down for several days it would also be necessary to flush another 10 - 20 bed volumes of water through to restore the pH to < 8.0 when flow was restarted. Although simple flushing readily solved the problem of elevated pH in the treated water, the time required to complete the flushing and water testing and the large volumes of water lost in the process were undesirable. Tests of the Bauxsol™ reagent before pelletisation showed no significant rise in pH after flushing with just two bed volumes of water and hence, the rise in pH associated with the Radium ProActiv™ pellets had to be due to cementitious agent (OPC) used as a binder. Initial tests showed that the amount of water that had to be flushed through the columns to get a stable pH below 8.0 could be lowered to < 20 bed volumes if the first two bed volumes of water flushed through contained a magnesium chloride plus calcium chloride brine but this still meant that restarting water treatment each time one column in the counter current flow system was exchanged, was unnecessarily complex, involved an undesirably long down-time and wasted a lot of water. The solution has been to develop a new pellet binder based on an adhesive polymer that is already approved for primary contact with human drinking water and will bind the particles of Radium ProActiv™ without coating the reactive surfaces (the effect is best pictured as like dew on a spider's web where the web is the adhesive and the mineral particles are the dew drops). Laboratory tests indicate that although the new adhesive based pellets are not as porous as the old OPC-based pellets, there is no apparent decrease in contaminant binding performance and, most importantly, there is no change in the pH of the water being treated after the first bed volume is passed through the columns. When final testing is completed in a few months time, it is likely that all OPC-based pellets used in commercial drinking water treatment operations will be replaced by the new adhesive-based pellets.

The OPC-based pellets have also been found to be very effective for removing uranium and thorium from acidic water. For example, when treating wastewater from a phosphate fertiliser production facility in Florida (initial pH = 1.6), the uranium concentration was lowered from 1,257 µg/L to < 2 µg/L and the thorium concentration from 75 µg/L to < 1 µg/L. Similarly, in a U.S. Geological Survey study of the treatment of acid rock drainage water at the Elizabeth Mine in Vermont (initial pH = 3.0), the uranium concentration was lowered from 2.86 µg/L to 0.97 µg/L and the thorium concentration was lowered from 2.43 µg/L to < 0.2 µg/L. However, tests on removing uranium from drinking water with a near-neutral pH show that treatment is less effective whether using OPC-based pellets, or the adhesive-based pellets, unless the water is first acidified to a pH ≤ 6.0 and the adhesive-based pellets are used. This procedure is necessary to convert anionic uranium carbonate and bicarbonate complexes to cationic oxide and hydroxide complexes that will more readily interact with the mineral constituents of Bauxsol™; in groundwater with a pH above about 6.0 the anionic uranium carbonate and bicarbonate complexes are usually dominant even at alkalinities of < 50mg/L $CaCO_3$ equivalent.

Removal of arsenic from drinking water

Data obtained by the US EPA from a large field trial at the Gilt Edge Mine Superfund Site in South Dakota showed that ordinary Bauxsol™ had an excellent ability to remove arsenic from acidic mine waters and that arsenic removal would continue for a long time; the arsenic concentration in untreated water was 35,000 µg/L and following a single treatment in 2001 the arsenic content in treated water was 3.1 µg/L in 2001, 3.7 µg/L in 2002, and < 0.4 µg/L in 2003 (the arsenic concentration has remained below the detection limit of 0.4 µg/L ever since); the pH of untreated water was 1.93 and for treated water ranged between 7.9 and 8.7. Similarly, the use of Bauxsol™ to treat wastewater from the phosphate fertiliser production facility in Florida lowered the arsenic concentration from 2,110 µg/L to 2 µg/L while raising the pH from 1.60 to 8.35; the concentrations of many other contaminants (particularly fluoride, phosphate and numerous metals) were also lowered to environmentally acceptable values. In commercial applications involving the treatment of industrial wastewaters, the Bauxsol™ was also easily able to lower arsenic concentrations to below 1 µg/L (e.g. Table 2) but all of these waters were well oxidised, at least slightly acidic (pH ≤ 6) before treatment, and the arsenic was all present as arsenate As[V].

Table 2. **Result of treating CCA (copper-chrome-arsenate) contaminated liquid from a timber treatment plant in Queensland, Australia**

Analyte	Before (mg/L)	After (mg/L)
Cu	19	0.005
Cr	6.0	0.007
As	2.8	< 0.001

The treatment used a Bauxsol™ containing 5% ferrous sulphate to lower the pH; this reagent is marketed as ViroBond™.

At this stage there were few data to show whether Bauxsol™ could also remove arsenite (As[III]) or whether it could remove any form of arsenic under the near-neutral to slightly alkaline conditions that normally exist in groundwater to be used for human consumption. Subsequent laboratory tests (Genç *et al.* 2003) confirmed the ability of unmodified Bauxsol™ to remove As[V] from acidic water but also showed that the removal of As[III] from acidic water was at least an order of magnitude less

efficient than the removal of As[(V)] and that the ability to remove either form of arsenic decreased increasingly rapidly as the pH of the water to be treated rose above about 7.0. Hence, there were two problems to solve if Bauxsol™ were to be as effective for removing arsenic from drinking water treatment as it was for removing arsenic from acid rock drainage water. Firstly, all the arsenic would need to be present as As[(V)] and secondly, the water would need to be slightly acidic. Converting all the arsenic to As[(V)] could be done by adding an oxidant, such as a peroxide, or a persulphate or a similar substance. However, chlorination, which is widely used in drinking water treatment to kill micro-organisms, also converts As[(III)] to As[(V)] and hence, no further action would be required if arsenic removal is done after chlorination. Acidification of the water could also be achieved by the addition of small quantities of hydrochloric acid but there is reluctance on the part of water treatment plant operators and regulators to add large volumes of any acid, even if interaction with the Bauxsol™ will raise the pH back into the acceptable range of 6.0 – 9.0. This limitation was overcome by developing activated and acid washed forms of Bauxsol™ (Genç-Fuhrman *et al.* 2004a,b,c,d) that are much more effective than activated or acid treated red muds. Acid washed Bauxsol™ is now preferred to activated Bauxsol™ because although it is only about 95% as effective as fully activated Bauxsol™, it costs less than one quarter as much to produce. The acid treated Bauxsol™ is one of the most effective materials known for binding arsenate (see comparisons in Genc-Fuhrman *et al.* 2004d) and the arsenate is bound sufficiently tightly that spent sorbent does not require disposal in a hazardous waste repository (Genc-Fuhrman *et al.* 2005). Major competing ions in order of decreasing influence are silicate, phosphate and sulphate (Genç-Fuhrman *et al.* 2004a, 2005) and with the local exception of silicate these ions are seldom sufficiently concentrated in well water to have a significant influence of arsenate removal; bicarbonate and chloride appear to have a negligible influence of arsenate sorption. We now had a very effective way to remove arsenic from potentially potable water but there was a new problem in that the very fine Bauxsol™ particles (> 80% are finer than 10 μm; McConchie *et al.* 2003) took too long to settle and were therefore not suitable for treating flowing water as would be required at most drinking water treatment facilities.

Because of the need to maintain pH conditions below about 6.5, the use of OPC-based pellets was not an option for producing coarse particles. Hence, Genç- Fuhrman *et al.* (2005) developed Bauxsol™ coated sand and activated Bauxsol™ coated sand and although these grains removed arsenic very effectively in flow-through columns, the columns had a short working life because most of the mass of the activated Bauxsol™ coated sand was inert quartz grains. Replacing the quartz sand by fine charcoal grains coated with acid washed Bauxsol™ increased the useful working life of a given mass of reagent in the columns because the lighter charcoal represented a much smaller proportion of the total mass. Now with the best Bauxsol™ coated charcoal columns, about 1,000 empty bed volumes, with an initial arsenic content of 100 μg/L, could be treated before the arsenic content in the treated water rose above 5 μg/L. However, this was still unsatisfactory because although the columns were much lighter and easier to handle, the reactive acid washed Bauxsol™ still only made up a small proportion of the content of the columns (about 10% - 12% at best); there was also an additional problem in that the very fine particles in the Bauxsol™ did not stick to the charcoal well and if the columns were agitated at all (e.g. by turbulent flow) some particles broke away giving the treated water a faint pink colour.

Table 3. Effect of using a siphon to pass 5 L of metal contaminated water with a near-neutral pH along 50 cms of wool fibre impregnated with 0.75 g of Bauxsol™ per 10 cm length

Analyte	Bauxsol™ type	Before (mg/L)	After (mg/L)	Removal (%)
Arsenic	AW	7.57	0.006	99.92
Aluminium	OB	156.5	0.095	99.94
Copper	OB	71.9	0.035	99.95
Cadmium	OB	4.34	≤0.001	>99.99
Iron	OB	3.16	0.027	99.15
Manganese	OB	53.4	≤0.001	>99.99
Zinc	OB	151.8	0.145	99.90
Nickel	OB	0.24	0.024	90.04
Lead	OB	0.14	≤0.001	>99.93

AW refers to acid washed Bauxsol™; OB refers to ordinary unmodified Bauxsol™.

The problem of getting coarse reagent into the columns was finally solved by using new adhesive-based pellets (marketed as Arsenic ProActiv™) and these were able to treat substantially more water for a given column volume; over 8,000 empty bed volumes of water with an initial arsenic content of 100 μg/L could now be treated before the arsenic content of the treated water exceeded 5 μg/L. However, the water to be treated still needed to have a pH no higher than a maximum of 7.0 (preferably 6.0 - 6.5) for treatment to be effective and there is still no way around this requirement other than mild acidification for water with a pH above about 7.0. Acidification to a target pH of 6.0 - 6.5 can be achieved by automated addition of controlled amounts of hydrochloric acid or sulphuric acid (the amount of sulphate added is too low for it to adversely affect arsenic binding as a result of competition for binding sites) or it is possible to add small amounts of ferrous sulphate or ferric sulphate solution. The use of ferrous sulphate or ferric sulphate solution has some advantages because not only does the iron generate hydrogen ions when it reacts to form ferric hydroxide but the freshly precipitated ferric hydroxide can provide some additional arsenic binding capacity; the Bauxsol™ reagent will readily mop up any excess iron remaining in solution.

Development of the adhesive-based pellets also made possible the production of Bauxsol™ and acid washed Bauxsol™ impregnated fabrics for use as filters that can remove arsenic and many other contaminants; for this purpose wool turns out to be the best fibre material we have tested, followed by cotton. Table 3 shows the effectiveness of Bauxsol™ and acid washed Bauxsol™ impregnated wool for removing contaminants from near water with a near-neutral pH. Impregnated fabric filters may be useful in applications for which pellets may not be the best option; e.g. disposable filters for household use to remove arsenic from drinking water in places such as Bangladesh.

Arsenate sorption by Bauxsol™ reagents also appears to be strongly time dependent, with acid washed Bauxsol™ (McConchie *et al.* 2002) reaching only 85% of its arsenic uptake potential after 21 days (Genç-Fuhrman *et al.* 2005); for some trace metals (e.g. McConchie *et al.* 1999) maximum sorption capacity is not reached even after 196 days. Such slow uptake kinetics complicate treatability studies but they also seem to be one of the reasons why once the arsenic (and many trace metals) is bound by Bauxsol™ it is very difficult to remove. Genç-Fuhrman *et al.* (2004b, 2005) showed that although arsenic removal increased with increasing leaching fluid pH, even an NaOH solution with a pH of 11.6 could remove only about 40% of the arsenic from arsenic saturated activated Bauxsol™. The remarkably low reversibility of As[(V)] sorption indicates that arsenic binding is not governed by simple ion exchange processes and

that it probably involves covalent bond development and the formation of inner-sphere complexes. Unfortunately, the slow reaction kinetics also mean that maximum arsenic bonding to Arsenic Proactiv™ pellets in flow through columns requires long residence times and the columns need to be large enough that they will remain operational without breakthrough for at least 3 weeks. Furthermore, if a single column is used, reagent at the input end will become arsenic saturated and as additional water is treated a front of nearly saturated reagent with a limited capacity to bind additional arsenic will move down the column effectively shortening the active column length and the residence time for water in the part of the column still capable of binding additional arsenic. Eventually a point will be reached when the active length of column remaining is not sufficient to lower the arsenic concentrations to the target values although a high proportion of the pellets in the column may retain more than half their original arsenic binding capacity. This problem is particularly significant in relation to arsenic binding by Bauxsol™ reagents because arsenic partitioning between the solid phases and the solution in contact with the solids is weak and hence, the arsenic concentration gradient on pellets in the column extends over a considerable length of the column. As a result of the limited arsenic partitioning within the column, the only practical way to ensure that most of the pellets in the column are close to saturation with respect to arsenic binding is to use at least three columns arranged in a counter current flow configuration as described for removing radium from drinking water. If acid washed Bauxsol™ pellets are used in such a counter current flow system and the water to be treated has a pH of about 6.5, then it could reasonably be expected that the pellets would be able to bind at least 0.5% of their own weight of arsenate.

Conclusions

Previous work has shown that caustic red mud can be treated by simple chemical procedures to produce a material (Bauxsol™) that has a near-neutral pH while retaining a good acid neutralising capacity and an excellent ability to trap and bind a wide range of inorganic contaminants. The results of laboratory studies and large-scale field trials summarised in this paper show that the Bauxsol™ reagent can be further refined and pelletised to produce a sorbent with an excellent ability to remove some very hazardous contaminants from human drinking water.

If the raw Bauxsol™ is water washed and pelletised it provides a very effective means for removing radium from water and lowering the gross alpha particle activity. Less than 0.1 g of refined Bauxsol™ (marketed as Radium ProActiv™) is required to lower the radium content of water from about 20 pCi/L to < 0.5 pCi/L (the limit for human drinking water is 5 pCi/L). The spent Bauxsol™ reagent will pass the TCLP leaching test with ease so that if the total activity of the spent reagent is kept below regulatory limits it can be safely disposed of in ordinary municipal landfill and does not require disposal in a radioactive waste repository. The need to keep the activity of the spent reagent below regulatory limits for municipal wastes, and not the radium binding capacity of the reagent, is the limiting factor controlling how much water can be treated per unit mass of Radium ProActiv™. If acid washed Bauxsol™ is pelletised and the water to be treated is acidified to a pH between 6.0 and 6.5, the reagent (marketed as Arsenic ProActiv™) can lower the arsenic concentration in water from above 1,000 μg/L to < 1 μg/L but the arsenic needs to be converted to As$^{(V)}$ for optimum performance. When used in columns set up in a counter current flow configuration, the Arsenic ProActiv™ can trap and bind about 0.5% of its own weight of arsenic and the spent reagent easily passes the TCLP test for classification as an inert solid. Removing arsenic from the spent reagent is very difficult and although the ease of removal increases with increasing pH, even a caustic soda solution with a pH of 11.6 can remove only about 40% of the bound arsenic. It is therefore easier to dispose of spent reagent than to attempt to regenerate it.

The red mud-based materials are already being used in commercial scale drinking water treatment and there is excellent potential for much wider application, particularly in developing countries and in remote areas or small communities elsewhere where it is not economically viable to establish large conventional water treatment facilities.

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