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TREATMENT OF AQUEOUS STREAMS CONTAINING STRONG OXIDANTS USING BITUMINOUS COAL

Fiona M. Doyle and Donna L. Bodine
University of California at Berkeley,
Department of Materials Science and Mineral Engineering,
551 Evans Hall#1760,
Berkeley, CA 94720-1760, USA.

ABSTRACT

Certain oxidizing contaminants, notably Cr(VI) and Mn(VII), are attenuated by reduction and sorption on organic matter in soils. Coals have some chemical similarity with this organic matter, and might be used on an industrial scale to treat effluents. We have studied the ability of acidic KMnO_4 to oxidize Upper Freeport, bituminous coal with concurrent sorption of the resulting Mn(IV) and Mn(II). The oxidizing ability of Cr(VI) was briefly investigated. The ability of the oxidized coal to sorb Cu^{2+} and Cd^{2+} was then studied, and compared with coal oxidized by hydrogen peroxide. The effect of oxidation treatment, metal ion concentration, and solution pH on metal uptake kinetics and coal loading was investigated. Potential applications for treating effluents containing oxidizing ions are discussed.

INTRODUCTION

The discharge of certain inorganic oxidants is strictly regulated because of the impact of oxidizing species on living organisms, and the inherent toxicity or carcinogenicity of some species, such as Cr(VI). Although many of these oxidants are known to be attenuated by reduction and sorption on organic matter in soils, this can produce contaminated soils and groundwater. Effluents and wastes containing problematic oxidants must be treated with reducing agents that can concentrate contaminants into treatable or disposable form. Unless they can be regenerated, reducing agents should be inexpensive and readily available. Since oxidizing contaminants are often associated with other species that are regulated because of their inherent toxicity, notably metals, it would be advantageous if these could be removed from solution at the same time.

Activated carbon appears to be effective for removing Cr(VI) from solution below pH 6(1). Bituminous coal was of interest as a potential reducing agent for several reasons. It is inexpensive and readily available. Coal has some chemical similarity with the organic material in soils that attenuates reducing agents; the more reduced state of coal makes it a very attractive reductant. Smith and Mapstone, for example, reported reduction of alkaline KMnO_4 by an Australian coal with precipitation of

MnO₂(2). Precipitates such as Mn are capable of sorbing soluble metal species, either reduction products of the oxidants, or other contaminants, thereby removing them from solution. Precipitates would be expected to nucleate on the coal, thereby facilitating subsequent solid/liquid separations. Furthermore, coal forms carboxylic and phenolic surface groups on oxidation; these can also complex and immobilize toxic metal ions. As discussed later, metal-laden coal might be treated by elution with acid, or by combustion and appropriate management of the resulting ash.

We have examined the ability of a bituminous coal to reduce KMnO₄ to Mn(IV) and Mn(II), which are adsorbed onto the coal surface, probably forming a manganese oxide surface layer. Because the oxidized coal and the manganese oxide might sorb other cations, the ability of coal samples oxidized by KMnO₄ to remove Cu²⁺ and Cd²⁺ (selected as model contaminants) from solution was studied. This behavior was compared with that of coal samples oxidized by H₂O₂. In addition, preliminary experiments on the reduction of Cr(VI) by the same coal are reported.

EXPERIMENTAL METHODS

Upper Freeport MV bituminous coal was obtained from the Troutville #2 Mine, Clearfield County, Pennsylvania and stored under argon after mining to prevent oxidation. The coal contained 17.59% ash, 27.05% volatile matter, 55.35% fixed carbon, 1.50% moisture, 0.68% phenolic oxygen and 1.01% carboxylic oxygen, on an as-received basis(3). The coal was ground in a ball mill, sieved, and the +250–200 mesh (63 to 75 μm) size fraction was stored under argon for use in this work.

The ability of the coal to remove Mn(VII) and Cr(VI) from aqueous solution through a combination of reduction and adsorption was investigated. Coal samples were stirred for 4 hours with 100 ml of pH 3, 8.42 x 10⁻³ M KMnO₄ solution at 25°C. 10g samples of coal were stirred for 4 hours with 100 ml of dilute K₂CrO₄ solution at pH 2.5 and 5.5. For all tests, suspension samples were filtered under vacuum, and the filtrate was analyzed using a Perkin Elmer 3110 atomic absorption spectrometer.

Metal uptake experiments used either raw coal, coal pretreated by 8.42 x 10⁻³ M KMnO₄ solution, using 100g of coal/liter, or coal pretreated by H₂O₂, which creates functional groups but no solid oxide, and was studied for comparison. 500 ml of 30% hydrogen peroxide (pH = 4.9) was used to pretreat 20 g of coal for about 2.5 hours, until there was no further effervescence, using an ice bath to prevent thermal decomposition of the H₂O₂. 15 g samples of raw or pretreated coal were shaken with 150 ml copper or cadmium sulfate solutions, prepared from 0.05M stock solutions with no pH adjustment, at 25°C. The partition of metals between coal samples pretreated by KMnO₄ and Cu or Cd sulfate solutions was studied from pH 1 to 13. For each experiment, 1 gram of coal was shaken with 10 ml of metal solution at 25°C for 2 hours, and the suspension was analyzed as described above.

RESULTS AND DISCUSSION

Removal of Oxidants by Coal

Table 1 shows the effect of the coal:solution ratio on the final Mn concentration after four hours of contact with a solution initially containing 8.4 x 10⁻³M Mn(VII). There is a minimum in the final concentration of Mn as a function of weight of coal added. The solution potential using 10 g of coal, which gave a final Mn concentration below

Table 1: Effect of coal concentration on removal of Mn(VII) by Upper Freeport coal from 100 ml of 462 ppm Mn(VII) ($8.4 \times 10^{-3}M$), pH 3 solution in 4 hours

Coal in 100 ml $KMnO_4$ solution (g)	1	3	5	10	12.5	15	20
Final Mn Concentration (ppm)	347	168	ND	ND	12	5	18

ND = not detected

Table 2: Effect of initial chromate concentration, $[Cr(VI)]_0$, and pH on total Cr(III) and Cr(VI) concentration, $[Cr]_{tot}$, after 4 hours treatment with Upper Freeport coal

$[Cr(VI)]_0$ (ppm)	pH ₀	$[Cr]_{tot}$ (ppm)	Final color
1200	2.5	800	yellow
1100	5.5	800	yellow
18	2.5	17	colorless
13	5.5	7	colorless

detection, was 1.22 V (SHE). Comparing this potential with the Eh-pH diagrams for the Mn-H₂O system(4) suggests that at moderate coal concentrations, Mn(VII) is reduced to insoluble MnO₂, whereas at higher coal concentrations, soluble Mn²⁺ is the final reduction product. X-ray diffraction of coal oxidized by KMnO₄ did not detect a crystalline phase, and no surface oxide layers were visible by SEM. Therefore, any manganese oxide that formed on the coal surface must be amorphous or microcrystalline.

Table 2 presents the results of preliminary studies on the removal of Cr using coal. Individual species were not analyzed, but the color after 4 hours, in conjunction with the Eh-pH diagram for the Cr-H₂O system(3), suggests that the very dilute samples were completely reduced to CrOH²⁺. Reduction consumes hydrogen, as demonstrated by the following "model" reaction, in which for simplicity, Cr(VI) is considered to oxidize elemental carbon to CO₂:



The resulting increase in pH would favor precipitation of some Cr₂O₃. The yellow color of the more concentrated solution indicates residual Cr(VI) using 10g of coal to 100 ml of solution. However appreciable Cr was removed from solution, probably due to partial reduction of Cr(VI), and precipitation of Cr₂O₃. Although much more work is needed to quantify the ability of coal to reduce Cr(VI), the preliminary results here demonstrate some capability that could be optimized with pH and Eh control.

Uptake of Cu and Cd by Oxidized Coal

Raw coal removed little Cu or Cd from solution. Figure 1 shows the effects of pretreatment with hydrogen peroxide and Mn(VII) on the removal of Cd from a $4.43 \times 10^{-3} M$ (498 ppm), pH=6 solution. Cd was removed rapidly initially, followed by little additional change in Cd solution concentration. Coal oxidized by KMnO₄ was more effective than coal oxidized by H₂O₂ in sorbing Cd. This suggests a significant difference in the surface conditions after the two different treatments. This could reflect the fact that the redox potential was about 1.22 V (SHE) during pretreatment of coal with KMnO₄, and only about 0.76V(SHE) during pretreatment with H₂O₂, and hence the coal would be expected to be more extensively oxidized after treatment with KMnO₄. However the differences could also be due to the formation of insoluble manganese oxide on the coal surface after treatment with

KMnO₄. The removal of Cu from 4.8 x 10⁻³ M solution was very similar. Because metal uptake was rapid, the kinetics were studied further. Figure 2 shows the Cu concentration in a solution initially containing 4.8 x 10⁻³ M CuSO₄, as a function of time in contact with coal pretreated with KMnO₄. All significant Cu uptake occurred in the first ten minutes (shorter periods could not be studied reliably, because of filtration limitations). This strongly suggests that metals could be sorbed *during* treatment of a waste containing both permanganate and other metals with raw coal.

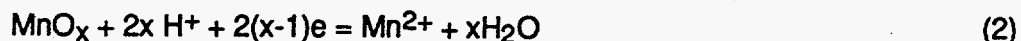
Figure 3 shows the uptake of Cu from a more dilute system (4.6 x 10⁻⁴ M, pH = 5.3) by oxidized coal. In this figure the parentheses (1) and (2), and corresponding closed and open symbols, designate different experiments, with starting times staggered to facilitate sampling. Coal pretreated by KMnO₄ was very effective in removing Cu from the more dilute system, eventually achieving 2.3 ppm residual Cu (8% of the original). Coal oxidized by H₂O₂ was ineffective.

Mn ions were released during sorption of metals by coal pre-oxidized by KMnO₄. Figure 4 shows the magnitude of this change in Cd and Mn concentration with time. The Cd in solution decreased somewhat in the first two hours after contact with oxidized coal, after which very little further sorption occurred. Some Mn was released into solution during Cd uptake, but although there is some ion exchange between Mn and Cd, the two changes are not related by an exact stoichiometric relationship. There was also no stoichiometric relationship between uptake of Cu and concurrent release of Mn. This suggests that metal ions are adsorbed by exchange with both Mn ions in the surface oxide and hydrogen ions in the functional groups on the oxidized coal surface.

Metal Uptake at Different pH

Cu and Cd uptake on coal pretreated by KMnO₄ was studied as a function of pH to identify whether bulk precipitation of metal hydroxides started competing with sorption, and assess whether metal uptake depends primarily on the coal surface functional groups generated by the different oxidation treatments, or is predominantly influenced by hydrolysis of the cations in solution. Figure 5 shows the change in concentration of Cu and Mn ions in solution, as a function of initial solution pH. Figure 6 presents the change in concentration of Cd and Mn ions. Very little Cu or Cd was removed at very low pH. The metal removals increased with increasing pH, steadily for Cu, and up to a plateau for Cd. Each system then reached a threshold where the metal was almost completely removed from solution, between pH 5 and 6 for Cu, and between pH 8 and 9 for Cd. These thresholds coincided with the pH's where bulk metal hydroxides precipitated during testing.

Figures 5 and 6 show that the amount of Mn released into solution decreased with increasing initial pH, and is not related to the uptake of Cu or Cd. Thus it is proposed that any manganese oxide present on the surface of coal pretreated by KMnO₄ undergoes simple, pH dependent reductive dissolution:



Under some conditions, Cu and Cd might sorb by ion exchange onto the MnO₂, but they can also be taken up by functional groups on the coal surface, or themselves form surface precipitates. The predominant mechanism is clearly pH dependent.

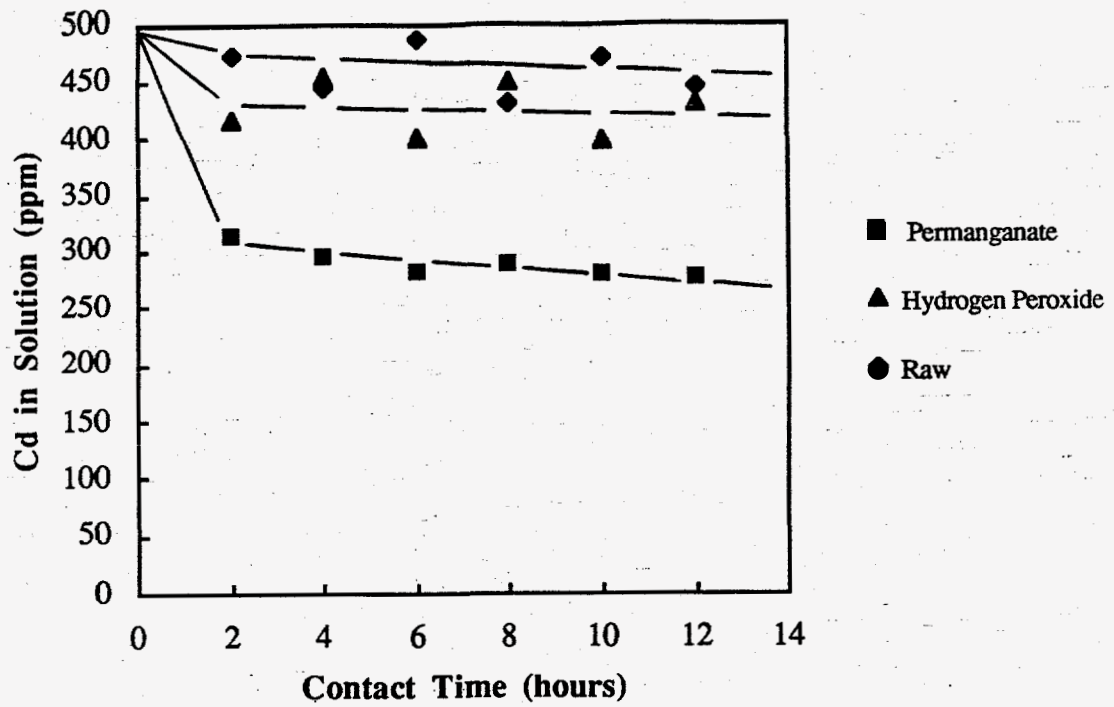


Figure 1: Effect of Upper Freeport coal oxidation treatment on removal of Cd from 4.43×10^{-3} M CdSO₄ solution (498 ppm Cd), initial pH 6.0.

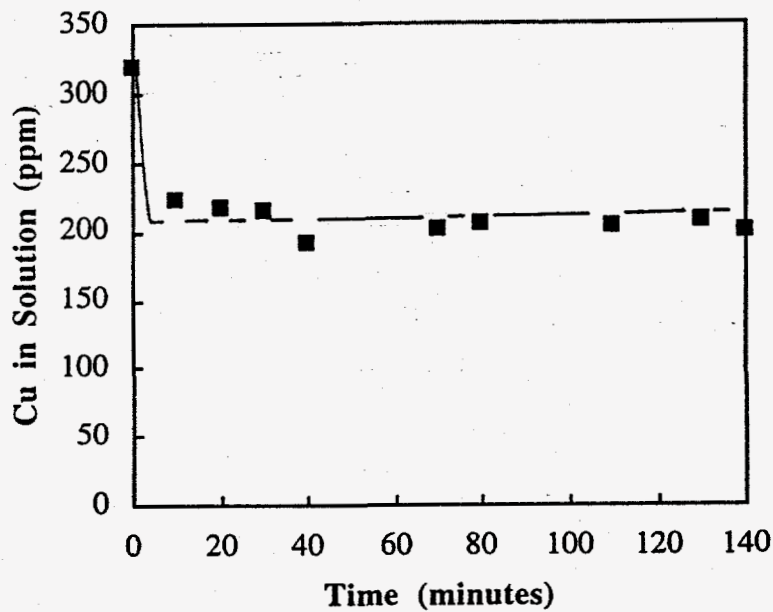


Figure 2: Removal of Cu from 4.8×10^{-3} M CuSO₄ solution (305 ppm Cu), initial pH 3.1 by coal pretreated with KMnO₄.

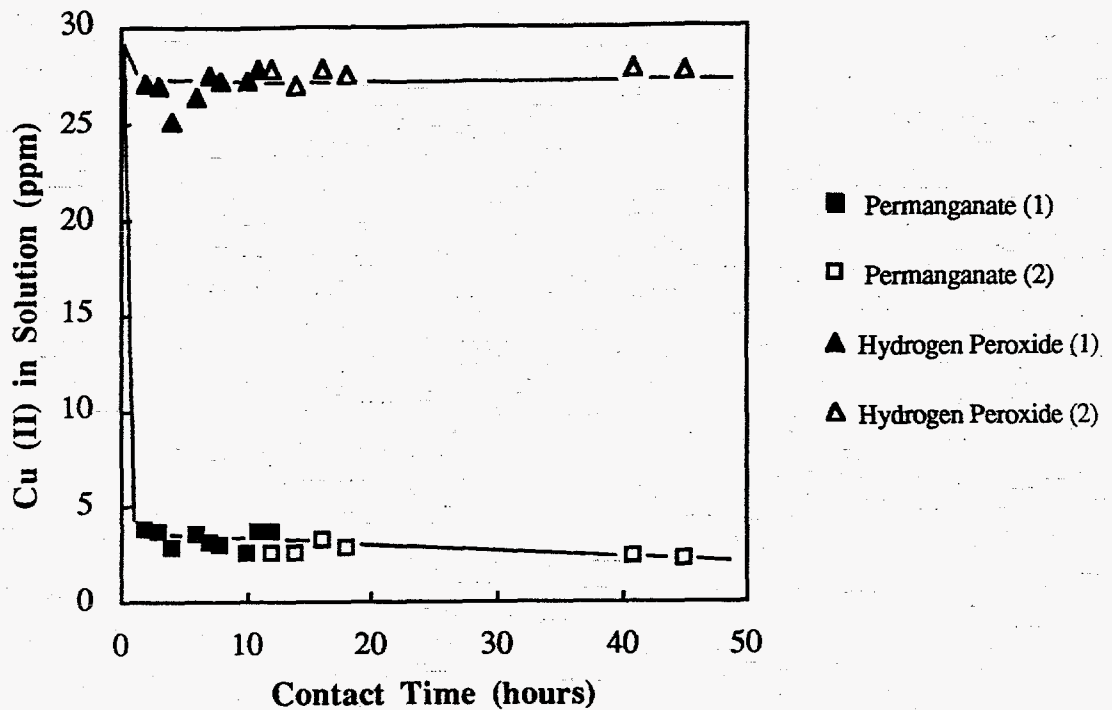


Figure 3: Effect of coal oxidation treatment on removal of Cu from 4.6×10^{-4} M CuSO_4 (29 ppm Cu), initial pH 5.3.

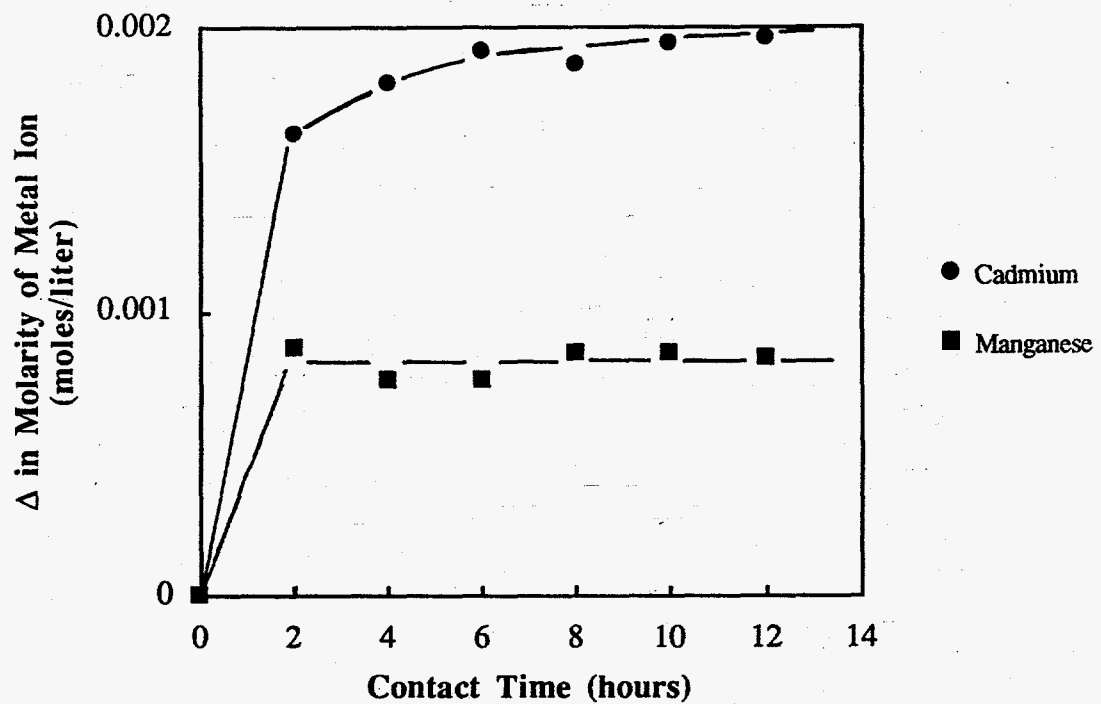


Figure 4: Magnitude of change in concentration of Cd and Mn ions during contact of KMnO_4 oxidized Upper Freeport coal with 4.43×10^{-3} M (498 ppm) Cd solution. (Cd concentrations decreased, Mn concentrations increased.)

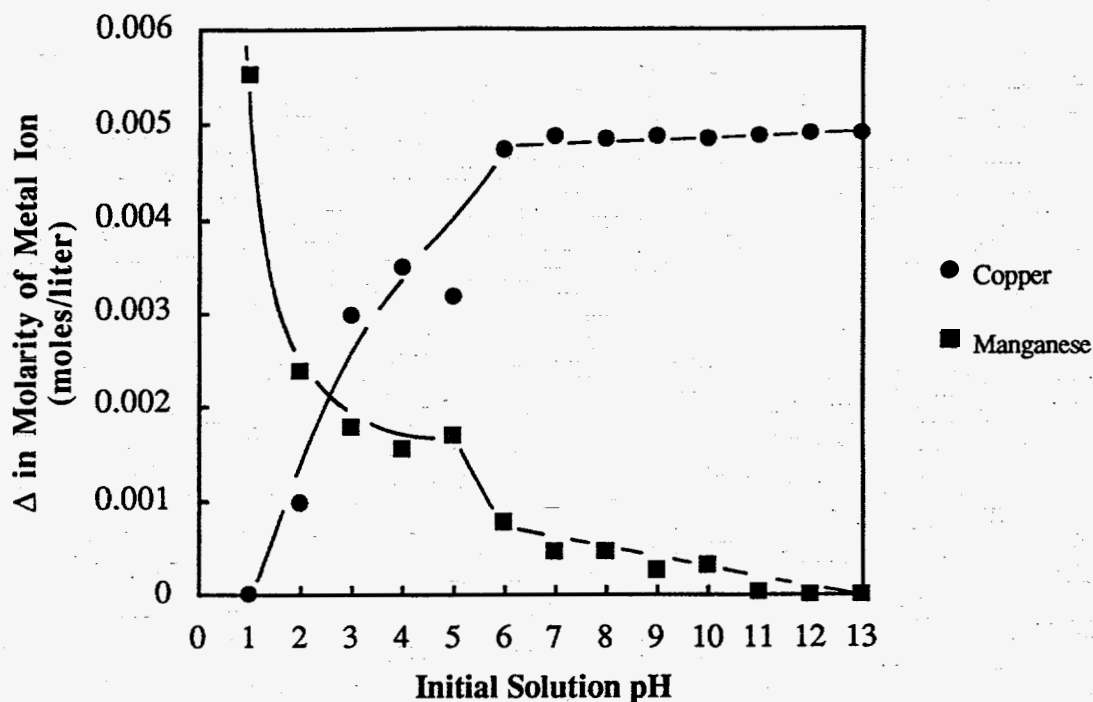


Figure 5: Magnitude of change in concentration of Cu and Mn ions during contact of KMnO_4 oxidized Upper Freeport coal with 4.9×10^{-3} M (312 ppm) Cu solution, as a function of initial solution pH.

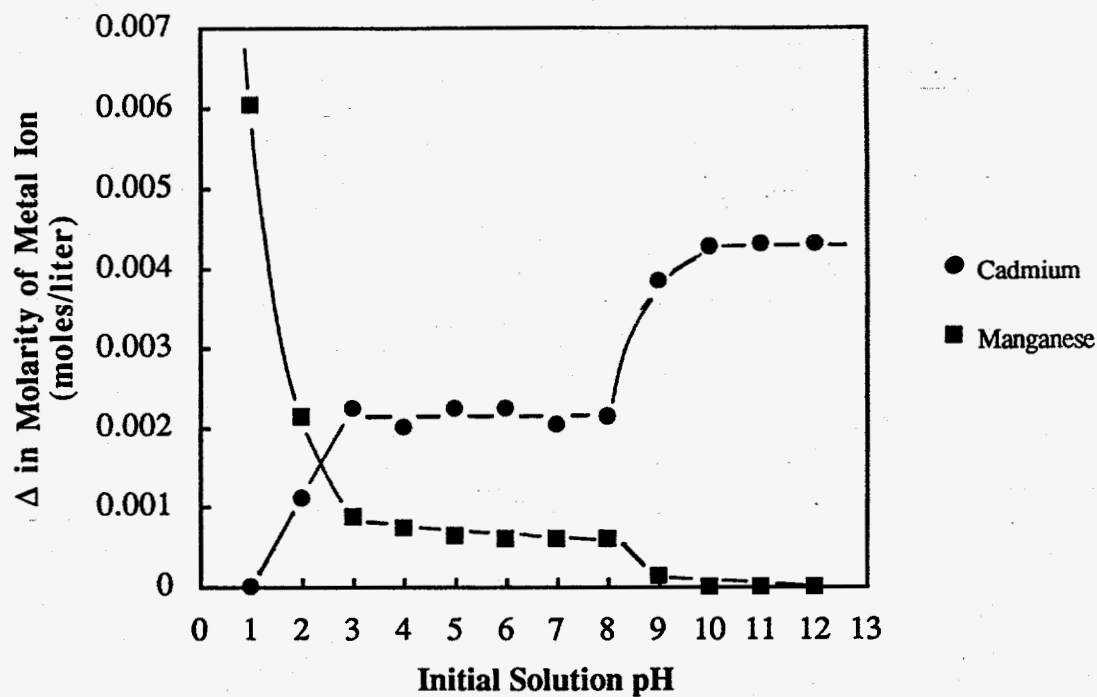


Figure 6: Magnitude of change in concentration of Cd and Mn ions during contact of KMnO_4 oxidized Upper Freeport coal with 4.3×10^{-3} M (486 ppm) Cd solution, as a function of initial solution pH.

Potential Commercial Application for Treating Effluents

Coal is able to reduce oxidizing contaminants present in aqueous solutions. The ability to sorb the resulting reduced species depends on the specific chemistry of the contaminants. After oxidation, the coal is able to remove toxic metals cations from dilute solution, with an efficacy that appears consistent with both the hydrolysis order of the cations, and their affinity for carboxylate groups, as observed in solvent extraction(5,6). It is not possible to predict the behavior of other contaminants, but the results here are sufficiently encouraging to warrant studying the ability of oxidized coal to adsorb other ionic species. Although coal could not remove all cations in single batch contacts, metal uptake appears to result from ion exchange with functional groups, and sorption on MnO_2 , if this is present, and the behavior is influenced by metal ion concentration and solution pH in a way that is consistent with an equilibrium being established. This suggests that significant removal of contaminants could be achieved by counter-current contacting, using columns or a series of continuously stirred batch reactors with counter-current decantation.

Two detoxification methods might be appropriate for metal-laden coal; it could be amenable to elution with acid, as is used for ion-exchange resins. Alternatively, the coal could be burned, causing the contaminants to report to the ash phase. If the ash released toxic metals easily, it could be treated by leaching, to recover a marketable metal product, and facilitate disposal. Alternatively, the toxic metals might report to inert crystalline or glassy phases in the ash, which could then be discarded without further treatment. The latter behavior is likely to be favored by higher combustion temperatures. Whether coal could be detoxified in existing combustion devices, such as power stations or cement kilns, or would require a dedicated facility, would depend on its composition, and many site-specific factors.

CONCLUSIONS

When $KMnO_4$ was reduced by coal, most of the Mn(VII) was removed from solution through reduction and adsorption of MnO_2 . When an excess of coal induced a very low solution potential, Mn^{2+} formed, and was less strongly sorbed. Coal pretreated by $KMnO_4$ could also take up Cu and Cd ions, with pH dependent release of Mn ions into solution, apparently by a combination of ion exchange and acid dissolution. Realistic water quality goals are likely to be achievable using counter-current contacting in commercial reactors. Coal was less able to reduce Cr(VI) and sorb the reduced species, presumably because of the lower potential needed.

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