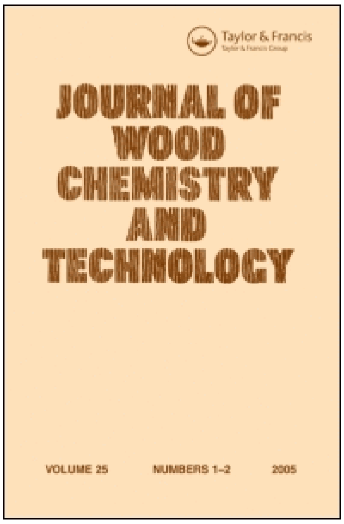

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

THE REMOVAL OF METALS AND RELEASE OF EDTA FROM PULP WASH WATER

Patrick Ager[a]; William D. Marshall[a]
[a] Department of Food Science and Agricultural Chemistry, Macdonald Campus of McGill University, Ste-Anne-de-Bellevue, Canada

To cite this Article Ager, Patrick and Marshall, William D.(2001) 'THE REMOVAL OF METALS AND RELEASE OF EDTA FROM PULP WASH WATER', Journal of Wood Chemistry and Technology, 21: 4, 413 — 425
To link to this Article: DOI: 10.1081/WCT-100108335
URL: http://dx.doi.org/10.1081/WCT-100108335

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 21(4), 413–425 (2001)

THE REMOVAL OF METALS AND RELEASE OF EDTA FROM PULP WASH WATER

Patrick Ager and William D. Marshall

Department of Food Science and
Agricultural Chemistry, Macdonald Campus of
McGill University, Ste-Anne-de-Bellevue,
QC H9X 3V9, Canada

ABSTRACT

The interaction of aqueous metal· EDTA complexes with magnesium metal or bimetallic mixtures of magnesium with either palladium or silver were optimized to remove metals (Cu, Fe and/or Mn) from solution with concomitant release of the EDTA ligand. The analyte metals were removed by both cementation on the surfaces of the excess magnesium metal and by precipitation as hydroxides. In all cases, the reactions were rapid and very efficient. The accelerators (Ag or Pd) were cemented on the surfaces of the magnesium more efficiently so that the excess of Mg granules could be reused to mediate more metals removal without apparent loss of reactivity.

INTRODUCTION

Environmental concerns associated with chlorinated bleaching agents (e.g. Cl_2 and ClO_2) have led to the increased use of more environmentally

www.dekker.com

benign oxygen-based bleaching agents such as ozone (O_3) or hydrogen peroxide (H_2O_2) in both elemental chlorine-free (ECF) and totally chlorine-free (TCF) pulp bleaching sequences. The versatility of H_2O_2 makes it one of the most widely used bleaching agents for both chemical and mechanical pulps. In addition to its central role in the brightening of mechanical pulps and recycled pulps, H_2O_2 is used to increase the effectiveness of the oxygen/alkali extraction stages in kraft pulp bleaching. The stability of H_2O_2 is a critical factor for the brightening of mechanical pulps. Inorganic ions, including Fe^{2+}, Mn^{2+} and Cu^{2+} catalytically decompose H_2O_2. The more troublesome Mn and Fe ions promote the rapid transformation of O_3 and H_2O_2 to nonselective hydroxyl radicals that degrade the cellulose fibers and decrease yields.[1–3] The ready availability of these metallic ions result in increased manufacturing costs and decreased product quality.

In consequence, it has become common practice to remove metal ions from the pulp prior the H_2O_2 bleaching stage of the process. Acid treatment has been considered to be an efficient treatment for controlling metallic ions[4] but supplemental Mg must be added back due to its removal during the treatment. On the other hand, the chelation treatment with EDTA or DTPA is much less efficient for the removal of alkali and alkaline-earth ions present in the pulp.[5,6] Recently, it has been reported[7] that the use of reducing agents in combination with DTPA is a cost-effective approach to increase the removal of harmful transition metal ions. To date, chelation treatment remains the method of choice for most pulp mills.

The chelating agents form water-soluble complexes with metal ions permitting them to be removed from the pulp by washing. In pulp mills operating in an open cycle, these ions are withdrawn continuously and are discarded with the waste water. With more stringent environmental controls and the move to effluent-free operations, the metal ions can be anticipated to accumulate in the processing water.[8,9] The impact of these metal ions, known as non-process elements (NPEs) have a generally negative effect under closed-cycle mill operations that include the buildup of scale, precipitate formation, equipment corrosion and the decomposition of bleaching chemicals.[10] Metal ions are only one component of a broad array of NPEs in mill effluent. Soluble organic materials, that can also mediate deleterious changes in bleaching efficiencies, will also accumulate in the recycled wash water and will have to be removed or otherwise controlled/inactivated. The quantity/availability of these organic NPEs might be controlled with a separation operation possibly by extraction with a benign, water immiscible solvent. However, the scope of the current report is limited to the description of a possible technique to control the availability of metal ions.

The ability to recycle a chelating agent can be anticipated to partially offset the cost associated with chelant extraction of metal ions from pulp. The electrolysis of a liquid stream containing metal ions from soil was investigated to release EDTA.[11,12] It was reported that post the quantitative mobilization of Pb using EDTA, up to 92% of EDTA was released by electrodeposition of the associated metals.[11] It provided a re-claimed EDTA stream that became available to treat additional contaminated soil.[12] The drawbacks of this technique include the rate of reaction, the selectivity of the reaction and the poisoning of electrode surfaces. An investigation of the extraction, recovery and biostability of EDTA for soil remediation demonstrated that cationic and anionic precipitants including calcium sulfide, were able to strip metal ions efficiently from their EDTA complexes and that the EDTA could be recycled up to 6 times.[13]

The use of zero-valent metals has been investigated[14,15] as a mean of removing metal ions from aqueous streams by cementation/precipitation. Zero-valent Fe was evaluated for the removal of dissolved metals from acid rock drainage. It was demonstrated that whereas certain ions became cemented to the surfaces of Fe^0, other ions were removed predominantly by precipitation.[14] In another study,[15] aqueous metal cations were extracted with an organic solvent (LIX-21) and the loaded organic phase was treated with a metal powder to selectively reduce the extracted metal cations and to promote their separation by stripping. The net result was that the organic phase was purified and could be recycled. Bimetallic mixtures have also been investigated to treat chlorinated organic contaminants. The addition of various accelerators to zero-valent metals increased both the efficiency of contaminant removal and the rate of reaction appreciably.[16,17]

The following series of reactions is considered to represent a reasonable mechanistic scheme that can account for the liberation of EDTA and the removal of copper, iron and manganese from aqueous media by cementation and/or precipitation.

$$\mathrm{M}\cdot\mathrm{EDTA}^{(4-n)-} \longrightarrow \mathrm{M}^{n+} + \mathrm{EDTA}^{4-} \tag{1}$$

$$n\mathrm{Mg}^0 + 2\mathrm{M}^{n+} \longrightarrow n\mathrm{Mg}^{2+} + 2\mathrm{M}^0 \tag{2}$$

$$\mathrm{Mg}^0 + \mathrm{H_2O} \longrightarrow \mathrm{Mg}^{2+} + 2\mathrm{OH}^- + \mathrm{H_2} \tag{3}$$

$$\mathrm{M}^{n+} + n\mathrm{OH}^- \longrightarrow \mathrm{Fe(OH)}_{n\,(s)} \tag{4}$$

Metal·EDTA complex is considered to exist in equilibrium with the free metal cation (M^{n+}) and the active form of the EDTA complexing reagent ($EDTA^{4-}$, Eq. (1)). The free metal cation (M^{n+}) can undergo a spontaneous redox reaction at the surface of the metallic magnesium (Eq. (2)) with the result that analyte (M^{n+}) is reduced to its metallic form (M^0) and becomes plated on the surface of the excess Mg^0. On thermodynamic grounds, all three metal analytes (Cu, Fe and Mn) are predicted to undergo spontaneous redox reactions with the more electropositive Mg^0. (The standard reduction potential, E^0, for the Mg^0/Mg^{2+} couple is considered to be ~ -2V). However, the rates of these reactions are dependent on the chemical identity of the analyte and the pH of the aqueous system. Concurrently, the zero-valent (metallic) magnesium can be hydrolyzed by water to liberate divalent magnesium cation, two equivalents of hydroxide and one equivalent of molecular hydrogen (Eq. (3)). The remaining metal cation can then combine with the liberated hydroxide to form sparingly soluble hydroxide precipitate (Eq. (4)).

The objectives of this work were to evaluate the ability of zero-valent magnesium (Mg^0) in the presence of Pd^0 or Ag^0 accelerator to strip Cu, Mn and Fe from their EDTA complexes. After removing the metal ions, the released EDTA was also to be determined. Finally, this technique was to be evaluated with a simulated post-chelation sample of wash water.

EXPERIMENTAL

Reagents

Aqueous Cu·EDTA, Zn·EDTA, Mn·EDTA and Fe·EDTA were diluted in double deionized water (D.D.W.) and used for the metal mobilization experiments. Aqueous Na_2EDTA and 0.1 M $Cr(NO_3)_3 \cdot 9H_2O$ were prepared from ACS reagent grade chemicals for the spectrophotometric determination of EDTA. Sufficient $AgNO_3$ or K_2PdCl_6 accelerator, to result in a 0.3 or 0.1% (w/w) loading respectively, were added to the magnesium (Mg^0) flakes (12–50 mesh). Sodium diethyldithiocarbamate (DEDC) and NaOH were used for the sample preparation and nitric (HNO_3) acid was used to adjust the pH. Chemicals, ACS reagent grade or better, were purchased from Aldrich Chemical Co., Milwaukee, WI (USA), Alfa Aesar, Ward Hill, MA (USA), Sigma, St. Louis, MO (USA), Acros Organics, Fairlawn, NJ (USA), or Fisher Scientific, Ottawa, ON (CANADA).

Metal Removal

Magnesium flakes (0.5 g, 12–50 mesh) were added to a 50 ml test tube prior to the addition of the accelerator K_2PdCl_6 [0.03–0.29% (w/w) as Pd^0/Mg^0] or $AgNO_3$ [0.01–2.74% (w/w) as Ag^0/Mg^0]. An aqueous mixture (10 ml) of Cu·EDTA, Fe·EDTA, Mn·EDTA and/or Zn·EDTA and 0.5 M $CaCl_2$ was added to the bimetallic mixture and reacted, at room temperature, for either 3 or 10 min. Post reaction, the solution was filtered through a 45 μm nylon Whatman filter paper and the filtrate, the precipitate and/or the rinsed and dried magnesium flakes were analyzed separately to determine the content of metals.

Quantification of EDTA

Prior to EDTA quantification, the sample was stripped of the more troublesome metal ions by adding excess NaOH to the wash water to precipitate Mn and Fe. The suspension was filtered to remove the precipitated metals and the filtrate was assayed spectrophotometrically after pH adjustment to ~5 with HNO_3 and DEDC added to precipitate Cu (if necessary). For aqueous filtrate from the Pd^0/Mg^0 or Ag^0Mg^0 reaction, treatment with NaOH/DEDC was not necessary. Metal ions were absent and the spectrophotometric method was applied directly to the filtrate (see below).

The concentrations of complexed and free EDTA were determined spectrophotometrically.[18] Sample filtrate (4 ml) was added to a test tube containing 1 ml of 0.1 M $Cr(NO_3)_3 \cdot 9H_2O$ solution. The pH of the solution was adjusted to 2–3 with 20% HNO_3, closed tightly and digested at 100°C for 15 min. A blank sample, containing 4 ml D.D.W. was treated analogously. After cooling, the absorbance at 555 nm, was measured against the sample blank and the concentration was estimated by means of a calibration curve.

Pulp Chelation Pretreatment

A sample of black spruce pulp was obtained from Paprican (Pointe-Claire, QC, Canada). The metal ion content was determined with a GBC 9100 atomic absorption spectrometer following the PAPTAC G.30P testing method.[19] Based on three replicate determinations, the mean concentration (±1 RSD) of manganese, iron and copper of the filtrate were determined to be 62.3 ± 1.5 μg/g; 79.7 ± 3.3 μg/g; and 2.3 ± 0.9 μg/g, respectively. The pulp sample was diluted in D.D.W. containing 5% (w/w) EDTA to a consistency of 3% and mixed in a Stomacher for 5 min. The pulp slurry was then heated in a water bath at 70°C for 60 min, cooled and the slurry was filtered through a Buchner funnel and pressed. An aliquot, 30 ml of filtrate, was treated with the Pd^0/Mg^0 or Ag^0/Mg^0 bimetallic mixture.

RESULTS AND DISCUSSION

EDTA Standard Experiments

Preliminary experiments with Mn·EDTA standard (Figure 1) indicated that the Mn (5.4 µmoles) was removed, virtually quantitatively, by either 0.5 or 1 g of Mg flakes reacted with ~5 mg K_2PdCl_6 or 0.3% (w/w) – Pd^0/Mg^0. Because differences were negligible, 0.5 g Mg was chosen for all subsequent experiments. Timed studies were conducted using either 3 or 10 min as presented in Table 1. A mixture of Mn·EDTA (5.4 µmoles), Fe·EDTA (5.6 µmoles) and Cu·EDTA (5.3 µmoles) was reacted with 0.3% (w/w) – Pd^0/Mg^0 for 3 or 10 min. The Fe and Cu were removed quantitatively within 3 min and the Mn was removed virtually quantitatively after 10 min and 96.7% after 3 min. Higher loadings of individual metal EDTA complex (Fe·EDTA, 16.7 µmoles; Mn·EDTA, 16.1 µmoles; Cu·EDTA 15.8 µmoles; or Zn·EDTA, 15.2 µmoles) were reacted, for 3 or 10 min, following the same procedure. For the higher metal ion loadings, the efficiency of the Mg^0/Pd^0 bimetallic mixture remained efficient for all three metals with greater than 99% removal after 3 or 10 min of reaction. Zn·EDTA was also investigated – the results demonstrated a virtually quantitative removal of the Zn within 3 or 10 min of reaction.

Based on these results, a reaction time of 3 min was deemed sufficient and was used for subsequent investigations.

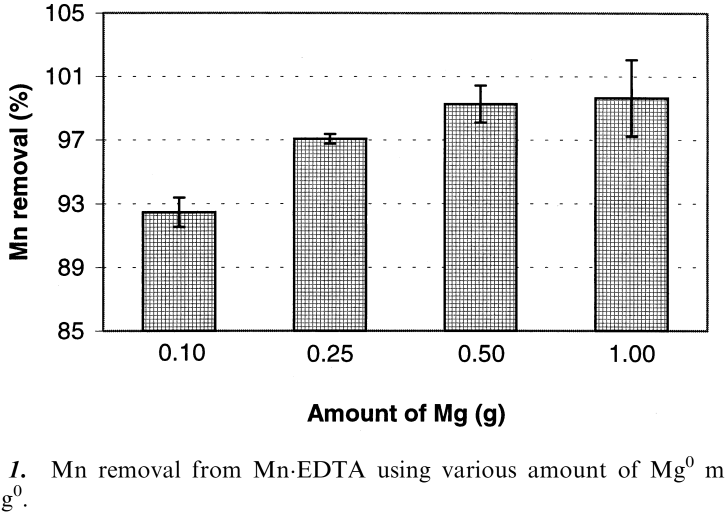

Figure 1. Mn removal from Mn·EDTA using various amount of Mg^0 metal as Pd^0/Mg^0.

Table 1. Efficiencies, with Time, for the Pd^0/Mg^0 Removal of Mn, Fe, Cu and/or Zn from a Solution Containing Mn·EDTA, Fe·EDTA, Cu·EDTA and/or Zn EDTA

	Pd^0/Mg^0 Reaction Time	
Metal-EDTA/μmoles	3 min ± 1 RSD[†]	10 min ± 1 RSD
Mixture M-EDTA		
Mn/5.4	96.7 ± 0.8	99.6 ± 5.8
Fe/5.6	N.D.[‡]	N.D.
Cu/5.3	N.D.	N.D.
Individual M-EDTA		
Mn/16.1	96.0 ± 0.8	N.D.
Fe/16.7	N.D.	N.D.
Cu/15.8	99.3 ± 3.2	N.D.
Zn/15.2	99.9 ± 4.7	99.9 ± 3.0

[†] Relative standard deviation (based on three replicate determinations).
[‡] None detected (< 0.025 μg/ml Cu, 0.02 μg/ml Mn and 0.05 μg/ml Fe).

In an effort to increase the rate of reaction, the influence of potential accelerators (palladium or silver) added with the Mg flakes was investigated systematically. Figures 2A and 2B present the results observed when a mixture of Mn·EDTA (5.4 μmoles), Fe·EDTA (5.6 μmoles) and Cu·EDTA (5.3 μmoles) was reacted, for 3 min, with Pd^0/Mg^0 or Ag^0/Mg^0 that had been prepared with various ratios of Pd^0/Mg^0 [0.03–0.29% (w/w)] or Ag^0/Mg^0 [0.01–2.74% (w/w)]. Figure 2A demonstrates that the Fe was removed efficiently from solution in the absence of Pd – only a slight improvement was observed with the addition of this accelerator. For Cu, an increase of approximately 11% was observed with the addition of 0.03% Pd^0 – for increased loadings of Pd on the Mg^0 surfaces, the removal remained constant. On the other hand, Mn removal was increased (~12%) by the addition of 0.03% Pd^0 but a further increase in the loading of Pd caused a slight decrease (not significant) in the efficiency of Mn removal. Excess Pd, added to the aqueous mixture, generated an unnecessary precipitate that reduced the metal removal efficiency. In Figure 2B, an aqueous aliquot of $AgNO_3$ was reacted with Mg flakes for 15 s before the addition of the mixture of metal·EDTA for 3 min. The results demonstrated a trend that, qualitatively, was similar to the results observed with Pd. The Fe was removed efficiently (97%) in the absence of Ag accelerator and quantitatively in the presence of Ag. The Cu and Mn followed a similar pattern with ~90% removal without Ag and virtually quantitative removal in the presence of Ag. The addition of

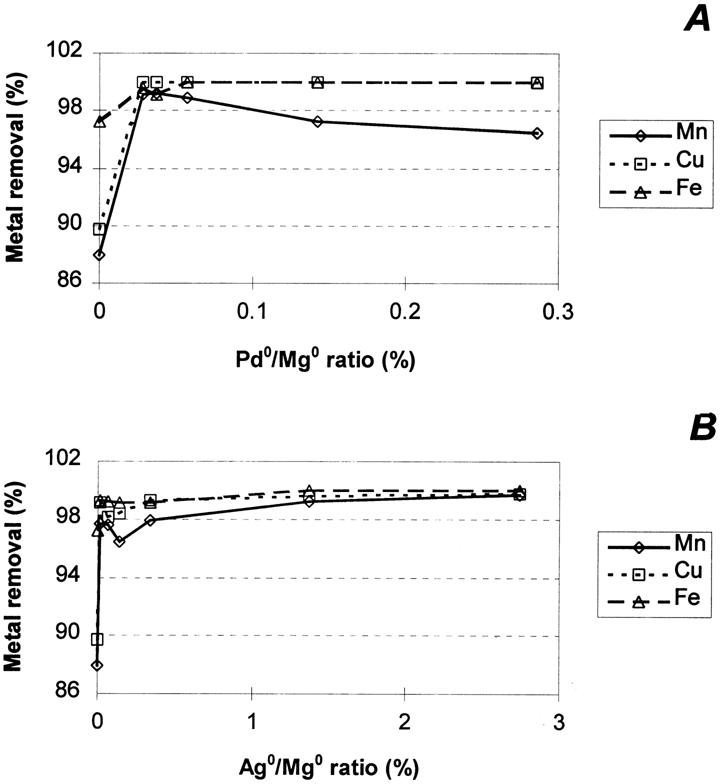

Figure 2. The role of the Pd^0 accelerator (*A*) and the Ag^0 accelerator (*B*) on the Mg mediated removal of Cu, Mn or Fe from metal·EDTA solution.

either Pd or Ag increased the removal of Mn and Cu ions but the Fe was removed virtually quantitatively without added Pd^0 and Ag^0.

A summary of results observed when a mixture of Mn·EDTA (5.4 μmoles), Fe·EDTA (5.6 μmoles) and Cu·EDTA (5.3 μmoles) were reacted with Pd^0/Mg^0 or Ag^0/Mg^0 for 3 min are recorded in Table 2. This table presents the efficiency of metals removal from solution, the quantities of EDTA that were recovered post stripping and the fate of the metals post reaction (precipitation as insoluble hydroxide or cementation, as zero-valent metal, on the surface of the excess Mg metal). However, the sum of the fraction of metal that had been cemented plus the fraction of metal that had been precipitated did not account for the entire substrate metal·EDTA complex that had been added to the solution initially.

Table 2. Metal Removal Efficiency and EDTA Recovery for the Pd^0/Mg^0 or Ag^0/Mg^0 Mediated Reaction with Cu·EDTA, Mn·EDTA and Fe·EDTA Complex During 3 min

Metal Ion/ µmoles	Metal Extracted ±1 RSD[¥] (%)	Metal Cemented ±1 RSD (%)	Metal Precipitated ±1 RSD (%)	EDTA Recovered ±1 RSD (%)
Pd^0/Mg^0 – 3 min				
Cu[1]	N.D.[§]	18.4 ± 1.1	66.5 ± 0.6	
Mn[2]	96.7 ± 0.8	10.3 ± 1.4	84.4 ± 0.4	90.1 ± 0.0
Fe[3]	N.D.	7.0 ± 3.1	87.4 ± 0.6	
Pd[4]	N.D.	24.4 ± 4.3	39.3 ± 2.6	
Ag^0/Mg^0 – 3 min				
Cu[1]	99.2 ± 3.5	30.8 ± 0.6	43.8 ± 1.7	
Mn[2]	98.7 ± 3.8	13.1 ± 1.1	72.3 ± 0.4	93.3 ± 0.0
Fe[3]	98.6 ± 3.3	10.8 ± 2.5	71.2 ± 1.6	
Ag[5]	N.D.	62.8 ± 1.7	11.4 ± 3.9	

[1] 5.3, [2] 5.4, [3] 5.6, [4] 12.6 and [5] 10.0 µmoles.
[¥] Relative standard deviation (based on three replicate determinations).
[§] None detected (< 0.025 µg/ml Cu, 0.02 µg/ml Mn and 0.05 µg/ml Fe).

Results have been expressed as percentages (%). The Pd^0/Mg^0 experiments demonstrate that the metals were removed virtually quantitatively from the aqueous medium and that Pd ion was not detected in the aqueous fraction.

In order to determine whether the metals were precipitated as metal hydroxides or cemented onto the Mg^0 surface, the filter paper and the Mg flakes were analyzed separately.

To ascertain if the metals had been precipitated, the content of the filter paper was dried, dissolved in 20% HNO_3 and quantified with flame atomic absorption spectrometry (F-AAS). An appreciable proportion of the Cu, Fe, Mn and Pd had been precipitated (67, 87, 84 and 39% respectively). Calcium seemed to play an important role in the metal transfer from the EDTA complexes. It was suggested that, at high pH, ligands including EDTA, NTA and succinate could be bound with calcium freeing up the heavy metals to form hydroxide or carbonate solids.[20]

The final pH (~10.5) provided a strong indication of the formation of $Mg(OH)_2$. It is well known that metals and their EDTA complexes are precipitated by the presence of sufficient quantities of hydroxide ion.[21] To verify if a portion of the metals had been cemented to the surfaces of Mg^0, the excess flakes that remained after the reaction were washed with copious quantities of D.D.W., dried in the oven, dissolved in 20% HNO_3 and analyzed by F-AAS. It was demonstrated that 18, 7, 10 and 24% of the Cu, Fe, Mn and Pd respectively had been cemented to Mg^0. The Cu and Pd seemed to have been cemented relatively efficiently.

The recovery of EDTA was determined using the Cr(III) assay. A strong correlation between the color developed at 555 nm and the quantity of EDTA added to calibration standards was observed (R^2, 0.9993). Interestingly, more than 95% of the EDTA was recovered from the aqueous metal·EDTA mixture after the treatment with Pd^0/Mg^0. The Ag^0/Mg^0 treatment was investigated with the same procedures. An analogous trend was observed – the Fe, Cu and Mn were removed efficiently (~98%) from metal·EDTA complexes. Ag ion was not detected in the aqueous fraction. Further investigations demonstrated that Cu, Fe, Mn and Ag were precipitated at 44, 71, 72 and 11% respectively. Cu, Fe, Mn and Ag were cemented to Mg^0 at 31, 11, 13 and 63% respectively. The Ag was cemented more efficiently than the Pd ion. At the same time, 93% of the EDTA was released from the metal·EDTA complexes. Both treatments with bimetallic mixture (Pd^0/Mg^0 and Ag^0/Mg^0) provided similar behaviors and metal removal efficiencies. The one difference resided in the cementation efficiency of the accelerator to Mg^0 with Ag^0 being cemented more efficiently than the Pd^0.

An attempt to reuse the Mg flakes after Pd^0/Mg^0 treatment was also performed (Figure 3). After each Pd^0/Mg^0 treatment, the flakes were washed with 1% HNO_3 for a short time and rinsed with D.D.W. The washed flakes were then used to remove the metals from fresh solution containing Mn·EDTA (5.4 μmoles), Fe·EDTA (5.6 μmoles) and Cu·EDTA (5.3 μmoles). The procedure was repeated for a total of 5 times. Figure 3 demonstrates that it was possible to recycle the Mg flakes up to 5 times and this with little decrease in removal efficiencies. Presumably, the number of cycles could

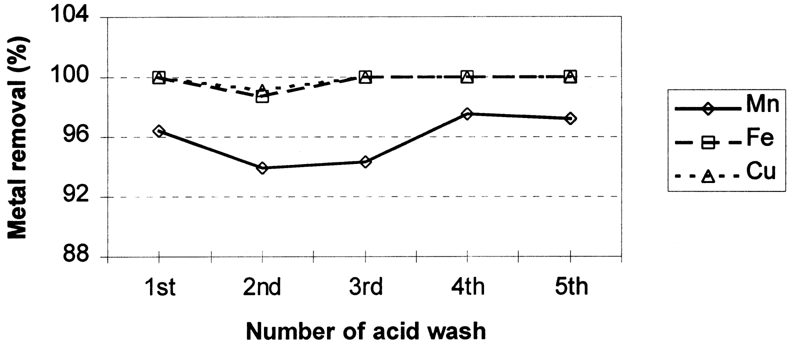

Figure 3. Recycling of Mg metal after 1% (v/v) HNO_3 washing.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

have been extended if the experiment had been initiated with a sufficient excess of Mg^0.

Simulated Wash Water Sample

The procedure was then applied to a simulated wash water from a black spruce pulp sample. As summarized in Table 3, the residual amounts of metals present in the filtrate were reduced to the limit of detection for the Fe and the removal efficiency was improved somewhat (90 to 95%) by increasing the reaction time, with Pd^0/Mg^0, from 3 to 10 min. The Pd ion was not detected in the filtrate. Both cementation and precipitation were

Table 3. Reactions, for 3 and 10 min, of Pd^0/Mg^0 or Ag^0/Mg^0 with Wash Water from Black Spruce Pulp

Metal Ion/ µmoles	Metal Extracted 1 ± RSD[¥] (%)	Metal Cemented 1 ± RSD (%)	Metal Precipitated 1 ± RSD (%)	EDTA Recovered 1 ± RSD (%)
Pd^0/Mg^0 – 3 min				
Cu[1]	N.D.[§]	N.D.	N.D.	
Mn[2]	90.4 ± 3.4	26.7 ± 2.3	47.4 ± 0.5	86.3 ± 0.0
Fe[3]	N.D.	41.6 ± 3.9	55.8 ± 1.0	
Pd[4]	N.D.	25.9 ± 1.6	70.7 ± 0.5	
Pd^0/Mg^0 – 10 min				
Cu[1]	N.D.	N.D.	N.D.	
Mn[2]	95.0 ± 6.7	23.7 ± 2.3	47.2 ± 0.5	84.4 ± 0.0
Fe[3]	N.D.	38.7 ± 4.2	52.8 ± 1.2	
Pd[4]	N.D.	26.6 ± 1.9	66.8 ± 0.6	
Ag^0/Mg^0 – 3 min				
Cu[1]	N.D.	N.D.	N.D.	
Mn[2]	54.3 ± 0.6	24.6 ± 2.3	28.2 ± 0.8	94.5 ± 0.0
Fe[3]	N.D.	45.3 ± 6.2	56.3 ± 0.0	
Ag[5]	N.D.	52.4 ± 0.8	45.5 ± 2.3	
Ag^0/Mg^0 – 10 min				
Cu[1]	N.D.	N.D.	N.D.	
Mn[2]	82.5 ± 0.6	28.5 ± 2.0	48.7 ± 0.4	95.0 ± 0.0
Fe[3]	N.D.	41.6 ± 3.9	52.6 ± 0.6	
Ag[5]	N.D.	60.3 ± 2.5	34.6 ± 2.5	

[1] 5.3, [2] 5.4, [3] 5.6, [4] 12.6 and [5] 10.0 µmoles.
[¥] Relative standard deviation (based on three replicate determinations).
[§] None detected (< 0.025 µg/ml Cu, 0.02 µg/ml Mn and 0.05 µg/ml Fe).

observed in these trials as well. There were no significant differences in the results after 3 or 10 min of reaction. The Mn, Fe and Pd were precipitated at ~47, 54 and 68% and cemented at ~26, 41 and 26% for both reaction times. Approximately 86% of the EDTA was recovered. The Ag^0/Mg^0 treatment proved to be somewhat less efficient in removing the Mn (~54% after 3 min) but increased to 83% removal after 10 min.

In both cases, the Fe was removed quantitatively. The cementation/precipitation results were not significantly different from each other for the 3 and 10 min reaction time except for the Mn due to the different extraction efficiency. The results for the Ag^0/Mg^0 trials were very similar to the results obtained with the Pd^0/Mg^0 treatment. Approximately 95% of the EDTA was recovered.

CONCLUSION

Magnesium metal was demonstrated to strip copper, iron and manganese from their metal·EDTA complexes and to remove them from solution by both cementation (on the surfaces of the excess Mg^0) and precipitation as hydroxides. The rates of reaction were increased by the presence of either Ag^0 or Pd^0 accelerator on the Mg^0 surfaces so that metals, at levels comparable to those in waste waters from treated softwoods, were removed efficiently within 3 min and virtually quantitatively within 10 min. The Pd^0 and Ag^0 accelerators were cemented to the Mg^0 surfaces somewhat more efficiently than the target metals so that excess Mg metal could be reused to mediate the destruction of more metal·EDTA complex without apparent loss of reactivity. The EDTA complexing reagent was recovered efficiently (but not quantitatively) and could have been recycled to complex more metals from the virgin pulp.

ACKNOWLEDGMENT

Financial support from the Natural Science and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

REFERENCES

1. Perng, Y.S.; Oloman, C.W.; James, B.R. Tappi J. **1993**, *76* (10), 139.
2. Colodette, J.L.; Rothenberg, S.; Dence, C.W. J. Pulp Pap. Sci. **1989**, *15* (2), J45.

3. Yokoyama, T.; Matsumoto, Y.; Meshitsuka, G. J. Pulp Pap. Sci. **1999**, *25* (2), 42.
4. Bouchard, J.; Nugent, H.M.; Berry, R.M. J. Pulp Pap. Sci. **1995**, *21* (6), J203.
5. Basta, J.; Holtinger, L.; Hook, J. APPITA 6th Intl. Wood Chem. Pulping Symp. **1991**, *1*, 237.
6. Lapierre, L.; Bouchard, J.; Berry, R.M.; Van Lierop, B. J. Pulp Pap. Sci. **1995**, *21* (8), J268.
7. Ni, Y.; Li, Z.; Jiang, Q.; Court, G.; Burtt, M. Pulp Pap. Canada **1998**, *99* (8), 77.
8. Ulmgren, P. Nordic Pulp Pap. Res. J. **1997**, *12* (1), 32.
9. Schmidl, W.; Frederick, Wm.J.; McAleer, M.; Rudie, A.W.; Gerbino, A.J.; Rorrer, G.L.; Yantasee, W. AIChE Symp. Series (Fund. Adv. Pulp Pap. Ind.) **1999**, *322*, 21.
10. Bygrave, G.; Englezos, P. Nord. Pulp Pap. Res. J. **1998**, *13* (3), 220.
11. Allen, H.E.; Chen, P.H. Environ. Prog. **1993**, *12* (4), 284.
12. Martin Jr., S.B.; Allen, H.E. Chemtech. **1996**, *26* (4), 23.
13. Hong, P.K.A.; Li, C.; Banerji, S.K.; Regmi, T. J. Soil Contam. **1999**, *8* (1), 81.
14. Shokes, T.E.; Moeller, G. Environ. Sci. Technol. **1999**, *33* (2), 282.
15. O'Keefe, T.J. PCT Int. Appl. patent WO 9116465 A1 (1991).
16. Zhang, W.-X.; Wang, C.-B.; Lien, H.-L. Catal. Today **1998**, *40* (4), 387.
17. Boronina, T.N.; Dieken, L.; Lagadic, I.; Klabunde, K.J. At http://www.engg.ksu.edu/HSRC/JHSR/v1_no6.html.
18. Flaska, H.A. *EDTA Titrations: An Introduction to Theory and Practice*, Pergamon Press: Oxford, 1964.
19. Standard testing methods (G.30P), PAPTAC.
20. Khudenko, B.M.; Gould, J.P. Water Sci. Technol. **1991**, *24* (7), 235.
21. Tünay, O.; Kabdasli, N.I. Water Res. **1994**, *28* (10), 2117.

Downloaded At: 12:17 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081WCT100108335