

# **A New Technology for the Treatment of Mercury Contaminated Water and Soils**

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## **ABSTRACT**

A new technology has been developed for the treatment of contaminated water and soils with lignin derivatives. It has been demonstrated that this technology can be used in the process of removal of high levels of mercury from water, and in the immobilization of leachable mercury in contaminated soils.

Lignin derivatives contain an abundance of oxygen-containing functional groups such as phenolic, alcoholic and enolic structures (-OH, -SO<sub>3</sub>H, C-O-C, C=O), which will form lignin-metal macromolecular complexes with high stability through ionic and coordinate covalent bonding. This feature is the basis for the application of lignin derivatives in the removal of metal contaminants from water and in the immobilization of leachable metal in soils or sediments. Tests have confirmed that lignin derivatives are capable of combining with a variety of metal ions including chromium, copper, lead, zinc, mercury, nickel and aluminum.

In the new water treatment process, lignin derivatives are dissolved in mercury contaminated water to complex mercury in an exceptionally stable form of a lignin-mercury colloid. The lignin-mercury colloid is then coagulated through the addition of a flocculating agent such as ferric chloride. Under optimized conditions, a clean effluent is produced with a residual mercury level of less than 1µg/L, together with a ferric sludge that is not leachable by TCLP (Toxicity Characteristic Leaching Procedure, EPA Method 1311).

In the new soil stabilization process, a new solid adsorbent of ferric-lignin is blended with mercury contaminated soil. This solid adsorbent can stabilize the soil by complexing with mercury and, thereby, greatly reduce the TCLP mercury of soil. The stabilized soil qualifies for disposal in a non-hazardous waste disposal site.

## INTRODUCTION

This study was undertaken in conjunction with an industrial site remediation project currently in progress. The site formerly housed a chloralkali plant using the mercury cell process, which has been dismantled. Material contaminated by mercury at the site includes soils, gravel, concrete, groundwater, and wastewater previously generated in the dismantled plant and from a contaminated soil washing facility.

At the remediation site, brown groundwater and surface water is currently treated in a precipitation process by using ferric chloride. It is well known that the brown color of groundwater and surface water is caused by dissolved humic and fulvic acids (HFA). Many investigators<sup>1</sup> have studied the color removal of water, which are widely practiced in municipal water treatment facilities. Interestingly, we find that the mercury contents of contaminated water can be greatly reduced from as high as 100 $\mu\text{g/L}$  to less than 0.5 $\mu\text{g/L}$  following the removal of HFA through a ferric precipitation process.

From particle size distribution experiments on mercury contaminated groundwater, this study has shown that most of the mercury exists in a Hg-HFA colloidal form but not in the free state. The addition of ferric chloride to groundwater causes the hydrolysis of ferric<sup>3</sup> to form ferric hydroxides due to their very small  $K_{sp}$  constants, leading to the formation of ferric flocs. Thus, the suspended colloids Hg-HFA are further coagulated to form a ferric sludge through sedimentation. This sludge can be separated in a clarifier to produce a clear effluent with less than 1 $\mu\text{g/L}$  mercury.

HFA exist in soil ubiquitously, and are formed by the biodegradation of organic matter, particularly plants, such as decayed lignin or tannins, etc. HFA consist of a mixture of complex macromolecules containing polymeric phenolic structures<sup>2</sup>. This feature gives HFA a great ability to chelate with metals, especially iron. This is the principle of applying ferric chloride to the removal of HFA and the mercury contaminants at the same time from the contaminated groundwater.

It is very important to recognize that HFA captures mercury contaminants in groundwater to form Hg-HFA colloid before ferric addition. This constitutes the fundamental principle of ferric chloride treatment in the removal of mercury from groundwater. However, there may not always be HFA present in industrial wastewater to combine with mercury contaminants. This could be the reason why the removal of free mercury contaminants from industrial wastewater at remediation sites is often inefficient by simply applying ferric chloride alone or combined with lime for pH adjustment. As one of the most important precursors of HFA, lignin<sup>4</sup> is a possible substituent for HFA. Especially the water-soluble lignin derivatives, such as lignosulfonates, are similar to HFA in that both can dissolve and disperse into wastewater and capture mercury to form stable complexes. The new technology uses lignin derivatives and ferric chloride to remove mercury contaminants from water, and to immobilize mercury in soil.

Kraft lignin and lignosulfonates are two types of commercially available lignin derivatives, which are produced as by-products in two different pulping processes

referred to as sulfate pulping and sulfite pulping respectively. The lignin derivatives contain an abundance of oxygen-containing functional groups, such as phenolic, alcoholic and enolic structures ( $-\text{OH}$ ,  $-\text{SO}_3\text{H}$ ,  $\text{C-O-C}$  and  $\text{C=O}$ ), which are capable of forming lignin-metal macromolecular complexes with high stability through ionic and coordinate covalent bonding.

Many methods for the treatment of metal contaminated wastewater teach the process<sup>5</sup> comprising precipitating metal contaminants from an aqueous media with a source of ferric ions, hydroxyl ions, and using a synthetic polymer as flocculent. A number of inventors<sup>6</sup> have applied the potential adsorption of lignosulfonates to the removal of organics successfully. Sanjay<sup>7</sup> et al. has patented an adsorbent preparation with humic acid, which can be used for the removal of contaminants and metals. In his US patent<sup>7</sup>, he also mentions an unsuccessful example for efficiently separating the lignin-metal complexes from the water.

This paper presents a new remediation technology, for which patents are pending<sup>8</sup>. The technology teaches a process of using lignin derivatives and a flocculating agent to remove metal contaminants from water, and of using a solid lignin-ferric adsorbent to stabilize leachable metals in soils.

## EXPERIMENTAL

### Particle Size Distribution of Colloid Hg-HFA in Groundwater

Light brown groundwater at the remediation site with the properties listed in **Table 1** was studied by adjusting pH with dilute HCl (about 10% by wt.) or NaOH (1N) over a wide range of 3 – 9, followed by filtration with a set of different pore-size filterpapers. The mercury content of filtrate in each case was determined with mercury analyzer (Cetac M6000). The data obtained are listed in **Tables 2** and **3**.

**Table 1. The Properties for Groundwater**

Items	Groundwater
Appearance	Light brown color with unhappy smell
pH	9.2
Total Hg ( $\mu\text{g/L}$ )	97
Total Solids ( $\text{mg/L}$ )	8460
Total Suspend Solids <sup>(1)</sup> ( $\text{mg/L}$ )	6
Total Suspend Solids <sup>(2)</sup> (%)	0.07
Conductivity ( $\text{microSiemens/cm}$ )	1475

Note:

(1) The residuals were obtained by filtration of groundwater through a  $0.45\mu\text{m}$ -pore filterpaper.

(2) Total Suspend Solids (%) =  $100 * \text{Suspend Solids (mg/L)} / \text{Total Solids (mg/L)}$ .

## General Procedure for Wastewater Treatment

The contaminated wastewater was subjected to mixing with the lignin derivatives prior to flocculation in the presence of coagulant, ferric chloride. It took about 1 - 5 minutes for uniformly mixing the wastewater (1000 parts by wt.) with the added lignin derivatives (0.1 to 100 parts by wt.). Following the addition of ferric chloride (0.1 to 10 parts by wt.) under agitation, the pH was adjusted by hydrated lime to about 5 – 7 leading to the flocculation of ferric sludge which contains lignin derivatives and the adsorbed mercury contaminants. The required amount of lignin derivatives, ferric chloride and hydrated lime are dependent on the properties of wastewater, such as, the level of metal contamination, hardness, pH, conductivity, etc.

After filtration, the dissolved mercury (size  $\leq 0.45\mu\text{m}$ ) content of the filtrate was less than  $1\mu\text{g/L}$ . The ferric sludge generated by this process demonstrates a great capacity of forming stable complexes with mercury contaminants. This feature can be utilized to immobilize the leachable mercury in Hg-contaminated soils or sediments<sup>9</sup>.

## Procedure for Removal of Diverse Metals from Water

An aqueous solution was prepared by mixing tap water together with each standard solution for aluminum, chromium, copper, lead, nickel and zinc. The contents for each dissolved metal ion are determined by ICP analysis (see **Table 6**). This aqueous solution (100 parts by wt.) was mixed with ammonium lignosulfonates (0.2 part by wt.) for one minute, followed by the addition of 3.2 parts weight of ferric chloride solution (40% by wt.). The pH of solution was adjusted with sodium sulfite (0.07 parts by wt.) and hydrated lime to 5.6. Allowing enough time for the sedimentation of ferric floc, 200ml of filtrate was passed through a  $0.45\mu\text{m}$ -pore filterpaper, and was taken for ICP analysis. After sampling, the pH of solution was further adjusted by soda ash to 8.6. The dissolved metal ions (size  $\leq 0.45\mu\text{m}$ ) remaining in the filtrate were determined by ICP analysis (see **Table 6**). The results show that five metals ions (chromium, copper, lead, mercury and nickel) are removed at pH 5.6, and that zinc ions was further removed by raising the pH to 8.6.

## Stabilization for Hg-Contaminated Soils

A high Hg-contaminated soil (100 parts by wt.) was uniformly blended with a solid lignin-ferric adsorbent (10 parts by wt.). The effectiveness for stabilization of leachable Hg in soil was determined by TCLP test once per week for a period of one month (**Table 7**).

## **RESULTS AND DISCUSSION**

### Particle Size Distribution of Colloid Hg-HFA in Groundwater

The data listed in **Table 2** and **3** were obtained from the experiments establishing the particle size distribution of colloid Hg-HFA in groundwater. Noticeably, the total

mercury content (97 µg/L) of groundwater (pH = 9.2) can be greatly decreased by the means of filtration only (**Table 2**). The removed amount of mercury is directly related to the pore-size of the filter paper. The smaller the pore-size of filter paper, the more mercury is removed. In addition, similar results were observed in other cases at pH 3, 5 and 7. Therefore, the experimental results show that Hg contaminants do not exist in a free state as molecules or ions, which can not be removed by filtration. The mercury exists in a complex form with HFA referred to as Hg-HFA colloid. The particle size of Hg-HFA colloid is dependent on the size of coordinated HFA.

**Table 2. Lab Data for the Effects of pH and Pore-size on Hg Contents<sup>(1)</sup>**

Pore-size of Filter Paper (Micron Diameter)	pH = 9.2 <sup>(2)</sup> Hg, µg/L	pH = 7.0 <sup>(3)</sup> Hg, µg/L	pH = 5.0 <sup>(3)</sup> Hg, µg/L	pH = 3.0 <sup>(3)</sup> Hg, µg/L
0.45	44.0	42.2	31.9	20.1
0.70	45.4	65.9	60.1	31.2
1.20	58.3	67.0	62.9	32.4
2.00	73.6	82.9	79.7	52.6
3.00	81.4	83.1	82.0	58.9

Note:

- (1) Total Hg content for the raw groundwater is 97 µg/L.
- (2) The raw groundwater.
- (3) The pH of raw groundwater was adjusted with HCl (1:1).

**Table 3. Colloid Hg-HFA Particle Size Distribution at Various pH Values<sup>(1)</sup>**

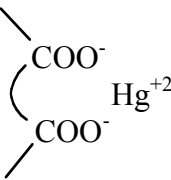
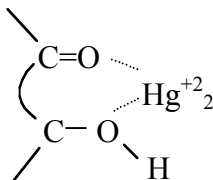
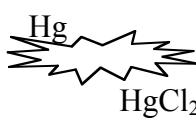
Particle Size Range (Micron Diameter)	pH = 9.2		pH = 7.0		pH = 5.0		pH = 3.0	
	Hg µg/L	%	Hg µg/L	%	Hg µg/L	%	Hg µg/L	%
≤ 0.45	44	45.4	42.2	43.5	31.9	32.9	20.1	20.7
(0.45, 0.70]	1.4	1.4	23.7	24.4	28.2	29.1	11.1	11.4
(0.70, 1.20]	12.9	13.3	1.1	1.1	2.8	2.9	1.2	1.2
(1.20, 2.00]	15.3	15.8	15.9	16.4	16.8	17.3	20.2	20.8
(2.00, 3.00]	7.8	8.0	0.2	0.2	2.3	2.4	6.3	6.5
> 3.00	15.6	16.1	13.9	14.3	15	15.5	38.1	39.3
> 0.45	53.0	54.6	54.8	56.5	65.1	67.1	76.9	79.3

Note:

- (1) The calculation results are based on the lab data listed in **Table 2**.

We believe, therefore, that most of mercury in the groundwater at the remediation site exists in a colloidal form through chemical bonding and/or intermolecular force. The colloid Hg-HFA would be a combination of the three patterns shown in **Table 4**.

**Table 4. The Bonding Types between HFA and Mercury**

	Chemical Bonded Hg Cation (primary force)		Physical Adsorbed Hg (secondary force)
Bonding Type	Ionic bond	Coordinate covalent bond	Intermolecular force (Van der Waals force)
Pattern			
Character	Mercury Fulvate or Humate	Mercury Complex	Fulvic or Humic Acid

Interestingly, about 55% of the total colloidal Hg with the size of  $> 0.45\mu\text{m}$  (**Table 2**) was adsorbed by suspended solids (size  $> 0.45\mu\text{m}$ , **Table 1**), which was only a small portion of total solids (about 0.07%) of groundwater at pH 9.2. The colored solids are predominantly HFA. This means that only a small portion of HFA has been combined with mercury. We believe HFA may have a great capability for further sorbing mercury contaminants. This could be the reason why the ferric sludge containing Hg-HFA colloids still has a great adsorption capacity of mercury<sup>9</sup>.

In fact, the ferric sludge obtained from groundwater treatment at the site is not leachable by TCLP test. It has a significant capacity to adsorb metal contaminants with very low leachability. This adsorption feature of ferric sludge has been utilized to immobilize leachable metal contaminants in soils and concrete fines<sup>9</sup>.

The pH adjustment is an efficient way to affect the colloid properties in solution. As a result, the dissolved mercury (particle size  $\leq 0.45\mu\text{m}$ ) content in solution is obviously decreased from 45.4% to 20.7% when pH is adjusted from 9.2 to 3 (**Table 2**). It shows that the small size of dissolved mercury tends to aggregate to become a large colloid at acidic conditions.

The colloid Hg-HFA is expected to have the negatively charged (such as HO<sup>-</sup> or Cl<sup>-</sup>) layer around the particle surface at pH 9.2, since the coordinate center of colloid is the positive mercury cation. Thus, the same negative charge on the surface of colloid Hg-HFA will retard efficient collision, leading to Brownian motion of organic colloids in water. Adding acid to neutralize the negative charge on the surface of colloid can destroy such kind of emulsion stability. The tiny colloid can be quickly converted to visible particles, which can be removed by filtration as a brown ferric sludge. Thus, the dissolved mercury (< 0.45µm) of groundwater is obviously decreased at acidic conditions (pH = 3). Additionally, we may be able to destroy the emulsion stability by electro-coagulation to collect the colloid mercury from groundwater directly.

### Mercury Contaminated Wastewater Treatment

Two types of Hg-contaminated wastewater #1 and #2 (**Table 5**) were obtained separately from two chemical processes previously used at the site. Both wastewater streams are clear, because of the absence of brown HFA, and have to be treated with lignosulfonates and ferric chloride. Following the general treatment procedure with lignosulfonates and ferric chloride, the dissolved mercury was substantially reduced to as low as less than 1µg/L in each case (see **Table 5**).

**Table 5. The Data for Wastewater Treatment**

Items	Wastewater #1		Wastewater #2	
	Before	After	Before	After
Appearance	Clear	Clear	Clear	Clear
PH	9.3	5.1	11.6	5.4
Total Hg (µg/L)	2490	0.67	498	0.61
Dissolved Hg (µg/L) Size < 0.45µm	1890	0.67	5.63	0.61
Suspended Hg (µg/L) Size (0.45, 2.0] µm	-----	0.0	68	0.0
Conductivity (microSiemens/cm)	1300	-----	800	-----

However, a further test on Wastewater #1 has shown that the dissolved mercury only can be reduced from 1890µg/L to about 720µg/L when using ferric chloride alone or combined with lime for pH adjustment. This clearly demonstrates that it is the lignin derivatives, which are responsible for the efficient mercury removal in the new described process.

The ferric sludge generated in the new treatment process contains stable complexes of lignin derivatives with the sorbed mercury, which is unleachable by TCLP test. The great capacity of adsorbing mercury for the ferric sludge can be further utilized to immobilize the leachable mercury in soils or sediments. The required amount of ferric sludge is dependent on many factors including the adsorption properties of ferric sludge, soil components, mercury contaminants and contamination levels of soils.

#### Removal of Diverse Metals from Water

Following the procedure for the removal of diverse metals from water, a prepared sample solution was treated (**Table 6**). The results show that the lignin derivatives are capable of combining with diverse metal ions including not only the heavy metals (chromium, copper, lead, mercury, nickel, zinc, etc.), but also the other metals such as aluminum. This is consistent with the theoretical prediction that the lignin derivatives are capable of forming quite stable complexes with polyvalence metal ions through the strong coordinate bonding. It is also the basis for the application of lignin derivatives to the removal of metal contaminants from wastewater and the immobilization of leachable metal in soils or sediments.

**Table 6. The Data for Treatment of Diverse Metal Ions in an Aqueous Solution**

Metals	Unit	MDL <sup>(1)</sup>	Before Treatment	After Treatment			
				pH = 5.6	Reduction (%)	pH = 8.6	Reduction (%)
Aluminum	µg/L	20	470	50	89.4	60	87.2
Chromium	µg/L	5	213	10	95.3	10	95.3
Copper	µg/L	5	2850	24	99.2	22	99.2
Lead	µg/L	30	120	< MDL <sup>(1)</sup>	> 75	< MDL <sup>(1)</sup>	> 75
Nickel	µg/L	10	210	40	81.0	100	52.4
Zinc	µg/L	5	7910	43	99.5	< 5	> 99.9

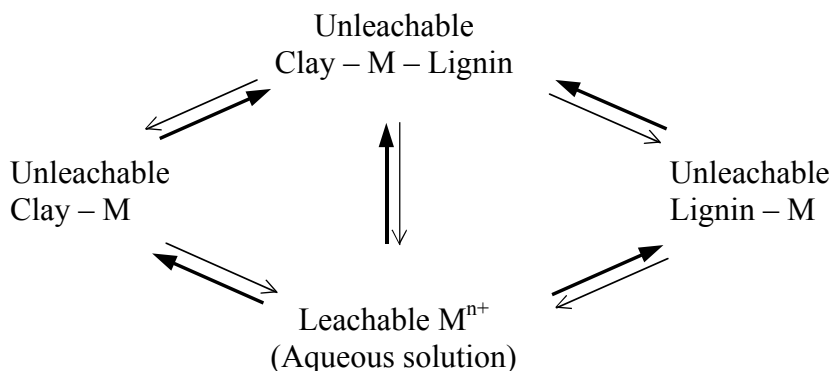
Note:

(1) Method Detection Limit for ICP analysis.

This example shows that the present method can successfully process the removal of diverse metal contaminants in wastewater to reach the acceptable levels (**Table 6**). It demonstrates a significant capacity of lignosulfonates to adsorb diverse metal ions in an aqueous solution. However, the reduction percentage for individual metal ions is expected to be further improved when other metal ions are absent.

#### Stabilization of Hg-Contaminated Soils

Adding small amounts of lignin derivatives to metal contaminated soils can increase the soil capacity of retaining metal ions against leaching. This could be attributed to the formation of metal complexes with lignin derivatives through strong coordinate bonding. While linking together, the negatively charged clay and lignin derivatives are neutralized by the positively charged metal ions. **Figure 1** shows that the presence of lignin derivatives in soil provides two more courses for the immobilization of leachable metal cations.



**FIGURE 1.** Schematic diagram for metal immobilization with lignin derivatives

At the remediation site, the mercury contaminated soils did not pass TCLP leachable mercury criteria and, therefore, could not be removed for disposal in non-hazardous sites. A new solid lignin-ferric adsorbent has been developed in a patented process<sup>8</sup>. It has demonstrated good sorption characteristics in the stabilization of mercury in soils (see **Table 7**). The results show that the solid lignin-ferric adsorbent can immobilize the leachable mercury in soil. The TCLP leachable mercury level of soil is greatly reduced from about 268 $\mu\text{g/L}$  to less than 50 $\mu\text{g/L}$ . The results further show that over 80% of leachable mercury are immobilized. The stabilization of immobilized mercury in soil was demonstrated by tracking over 30 days (**Table 7**). Therefore, the present technology can effectively stabilize leachable mercury in contaminated soil to a satisfactory level.

**Table 7. The Data for Stabilization of Leachable Hg in Soil**

Sample	Before Treatment	After Treatment				
		15 min.	7 days	14 days	21 days	30 days
Soil pH <sup>(1)</sup>	11.8	11.8	11.4	11.5	11.2	11.0
TCLP <sup>(2)</sup> extract pH	6.1	6.4	7.0	6.4	6.4	7.0
Total Hg in TCLP extract ( $\mu\text{g/L}$ )	268	76.4	35.0	28.0	35.8	39.3
Reduction of Leachable Hg (%)	-----	71.5	86.9	89.6	86.6	85.3

Note:

- (1) 5.0-g soil sample in 96.5ml deionized water.
- (2) US EPA Method 1311.

## CONCLUSION

A new technology has been developed to utilize the capability of lignin derivatives to strongly complex with various metals. This technology has led to an efficient and economical method for the removal of mercury (or diverse metal) contaminants from highly metal contaminated wastewater by the addition of lignin derivatives and a coagulant, such as ferric chloride. The ferric sludge generated in the new process contains the stable complexes of lignin derivatives with the adsorbed mercury, which is unleachable by TCLP. The great capacity of adsorbing mercury for the ferric sludge can be further utilized to immobilize the leachable mercury in soils or sediments. In addition, a new adsorbent of solid lignin-ferric has demonstrated great adsorption capacity, which can be directly utilized to immobilize the leachable mercury in contaminated soils.

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