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Immobilization of chromium-contaminated soil by means of microwave energy

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Abstract

To reduce the amount of hazardous wastes contaminated by heavy metals, a new technology to immobilize heavy metal ions is desired. Microwave (MW) technology which can be used to vitrify the contaminated soil wastes and immobilize the heavy metal ions for this purpose to satisfy the leachate test standard. We found that 90% + of the chromium-contaminated soil went through the glass/ceramic transformation and was thus vitrified after being radiated with MW for 60 min. The chromium ion (Cr^{6+}) concentration in the leaching test of all the vitrified soil samples is less than 1 mg/l, below the USEPA regulatory limit of 5.0 mg/l. This technology may become a major treatment method for hazardous wastes if the large-scale field test proves to be successful. In this paper, we will present the experimental conditions, the results and the future projects. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Microwave technology; Immobilize; Vitrify; Chromium; Soil

1. Introduction

The US Resource Conservation and Recovery Act (RCRA), and the Hazardous and Solid Waste Amendments (HSWA) contain provisions aimed at reducing the use of land disposal for the hazardous materials [1,2]. It has been well-documented that some of the successful solutions to toxic waste management are through waste detoxification. However, there are certain hazardous wastes to which the decontamination process has not yet been formulated; consequently, these wastes will continue to be managed by land

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disposal until new detoxification technologies are developed. For example, up until the development of microwave (MW) decontamination, chromium-contaminated soils used to be one of the most difficult toxic wastes to be managed. The contamination of these toxic wastes poses a serious healthy threat to the general population via water and food ingestion [2,3]. The development of a cost-effective technology for treatment of these hazardous heavy metal wastes therefore has become increasingly important and essential.

Chronic exposure to chromate dust will result in high incidence of respiratory diseases such as lung cancer. Animal data collected from excessive oral administration of Cr have documented cases of growth retardation, liver and kidney failures. One of the well-documented cases of Cr toxicity is found in Jersey City, NJ, USA. In some regions of the city, the Cr concentration has exceeded 50 000 mg/l; since then, Jersey City has been designated as one of the superfund sites by the Environmental Protection Agency (EPA). Several studies have shown that the toxic effect of Cr is almost entirely associated with the hexavalent (Cr^{6+}) materials [1,2], with a few cases associated with trivalent chromium (Cr^{3+}).

MW radiation is a form of electromagnetic radiation, with frequency ranging from 100 MHz to 300 GHz. The electric field interacts with polar materials and the magnetic field reacts with charged material [4–8].

There are three classes of mediums involved in a MW radiation processing system: conductors, insulators, and dielectrics [9–11]. Metallic conductors such as copper, brass, aluminum and silver, reflect MW except the metal with sharp edges. This reflective property is used to contain and direct MW; for example, wave-guides in a MW oven are usually made of brass or aluminum. Insulators either reflect or transmit MW and generally absorb only a small amount of MW energy. Teflon and polypropylene (PP) for example are utilized as part of the MW system. Dielectrics have properties in between conductors and insulators. In the field of MW radiation, dielectrics absorb MW energy in varying degrees.

Dielectric constant, a misnomer, plays an important role in determining the MW energy absorptive properties of these materials. There are several factors that affect the value of the dielectric constant, for example, moisture content, temperature, and geometric factors [3,7,8,11–15].

The pollution of Cr is just one of several heavy metal toxicity that deserve serious attention. It has been designated as standard material used in the process of MW decontamination. The final analysis of this new technology is based on the US EPA Toxicity Characteristic Leaching Procedure (TCLP).

2. Experimental

2.1. Preparation of chromium-contaminated soil

(1) Preparation of 0.1 M K_2CrO_4 solution by adding distilled water as solvent; (molecular weight of $\text{K}_2\text{CrO}_4 = 194.2$ g/mole). (2) Weigh 140.0 g of soil. (3) The

volume of K_2CrO_4 solution taken depends on the degree of contamination (for example, 260 mg/l needs 7.0 ml of 0.1 M K_2CrO_4 solution and to be added to 21.0 ml of solution). (4) Pour K_2CrO_4 solution 21.0 ml over 140.0 g soil and stir well until the soil is wet (the soils used for experiments are silt and clay mixture). (5) Place the wet contaminated soil into MW oven and heat until dry. (6) Transfer the dry soil into beaker, then put the beaker in the sand bed which is covered with aluminum foil on the outer surface. (7) Place the system contain Cr-contaminated soil into MW radiation field (the MW radiation system used for experiment is Sharp R-8580A with frequency 2450 MHz).

2.2. Additives

2.2.1. GAC—granulated activated carbon (Merck, Article #2514, diameter 1.5 mm)

There were two different sizes of beakers (reactors) used in the experiments. The one is 100-ml size beaker with the exposed surface area 5.0 cm², and the other one is 150-ml size beaker with the exposed surface area 7.5 cm². Weight 140 g of Cr-contaminated soils prepared as described before in this study.

GAC was placed uniformly on the top of soils. The reactor then was put into the sand bed covered with aluminum foil on the side and bottom of the reactor. The experiments are run in the MW system at 'HIGH' power condition.

2.2.2. Iron wires

Iron wires (IW) were inserted into the contaminated soil to determine whether or not they can cause a deeper penetration of MW radiation absorption and how many IW were needed to achieve this purpose. The diameter of the IW was small, around 0.1 cm. By applying different length of IW in the soil (IS) and exposed above the soil (OS), the effects of these parameters are also run in the MW system at 'HIGH' power condition (800 W/h).

After the reaction time, the beaker (reactor) was cooled down to room temperature. The tests then were set up to determine the leaching value of the final products—in vitrified and non-vitrified parts. All the before and after treated samples were analyzed by the US EPA TCLP. Atomic Absorption (PE 2380) was the instrument to be used for analysis of leaching concentration of chromium. The accuracy for this TCLP/AA method is controlled by 99.7% or higher.

Table 1
The conditions of the GAC–MW treatment in Figs. 1–3

Figure number	[Cr ⁺⁶] concentration (ppm)	GAC weight (g)/height (cm)	Size of reactor (ml)	Exposed area of reactor (cm ²)	Reaction time (min)
Fig. 1	260	6–15/0.5–1.8	150	7.5	50
Fig. 2	260	6–15/0.5–1.8	100	5.0	50
Fig. 3	260	10/1.2	100	5.0	0–55

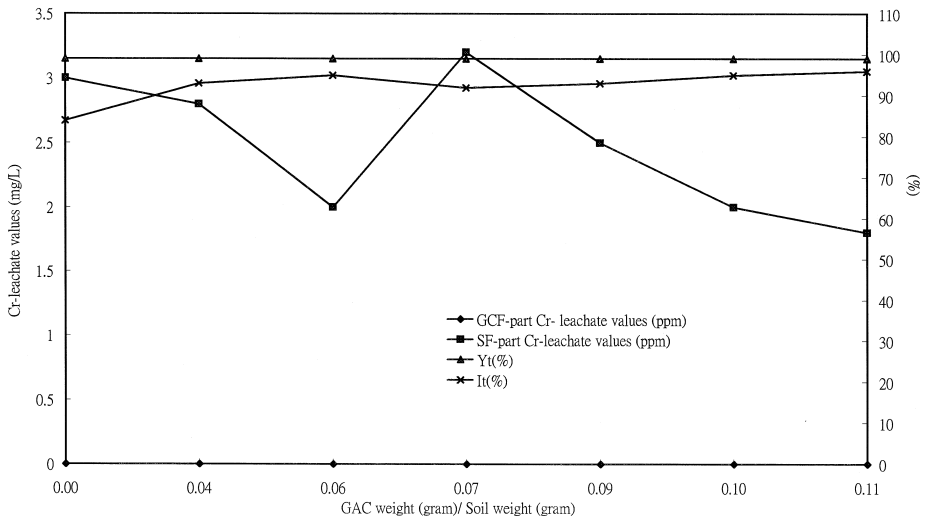


Fig. 1. Results of Cr-contaminated soil for a reactor size—150 ml with additives GAC and reaction time $t = 50$ min.

Y_1 is the non-leaching efficiency as a function of time; I_t is the efficiency of immobilization after t -minutes of treatment; C_s is initial chromium-concentration (mg/l); C_o is the leaching value before treatment; and C_t is the leaching value after t -minutes of treatment.

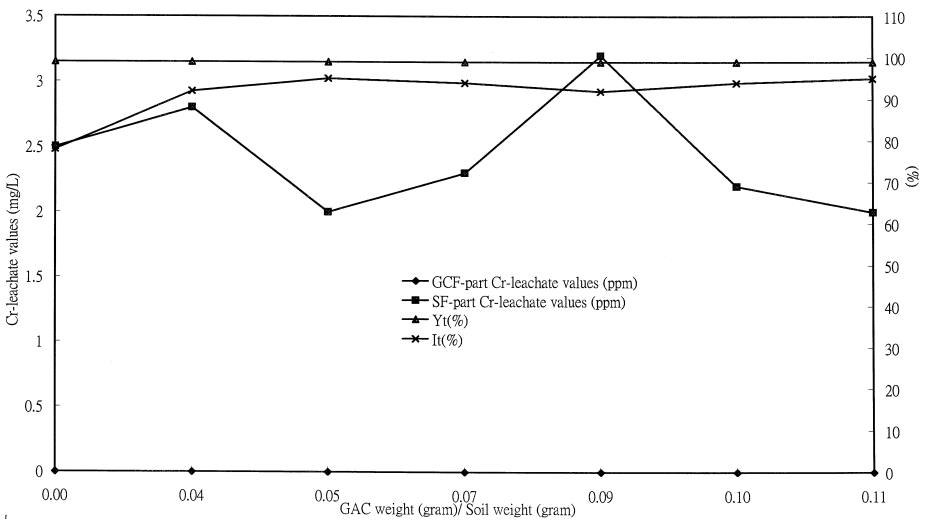


Fig. 2. Results of Cr-contaminated soil for a reactor size—100 ml with additives GAC and reaction time $t = 50$ min.

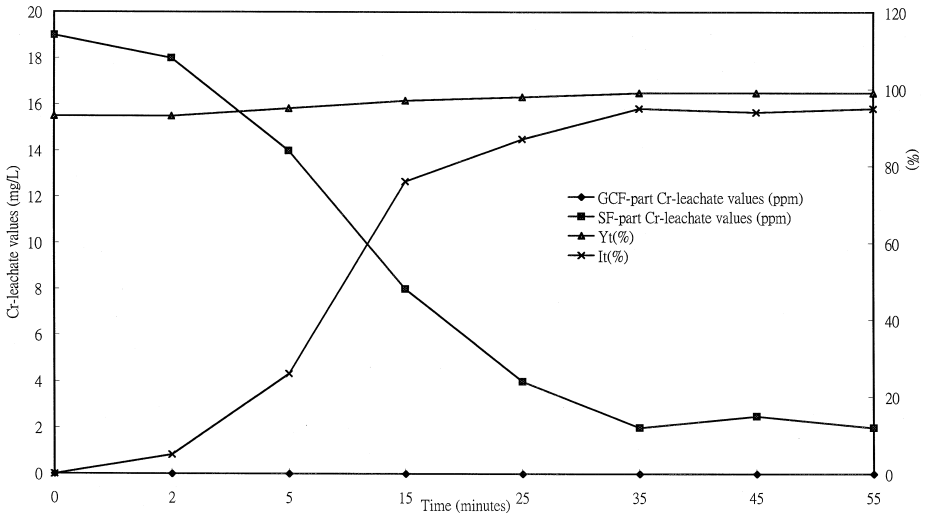


Fig. 3. Results of Cr-contaminated soil for additives 1.0 g of GAC with variable reaction time, *t*, from 0.0 to 6.0 min.

Table 1 shows the experimental conditions of the GAC–MW treatment for the results of Figs. 1–3. Table 2 shows the experimental conditions of the IW–MW treatment for the results of Figs. 4–7.

3. Results and discussion

There are two final products generated from the MW treatment, a vitrified glass/ceramic formation (GCF), and a non-vitrified soil formation (SF). The analysis will therefore be based on these two products. On occasion, only the SF product was observed, which suggest only the dehydration process had occurred.

The control leaching-value was determined from soil with Cr⁶⁺ concentration of 0 mg/l. The soil samples were divided into 0, 26, 130, 260, and 520 mg/l. The leaching values were compared before and after the MW treatment. The samples were treated until the leaching values were below the USEP regulatory limit (less than 5.0 mg/l) for chromium. It is also found that the standard deviation for the experiments is less than 0.1%

Table 2
The conditions of the IW–MW treatment in Figs. 4–7

Figure number	[Cr ⁺⁶] concentration (ppm)	Number of IW	IS (cm)	OS (cm)	Size of reactor (ml)	Exposed area of reactor (cm ²)	Reaction time (min)
Fig. 4	260	1–6	6.5	1.0, 1.5, 2.5	100	5	50
Fig. 5	260	1–6	7.5	1.0, 1.5, 2.5	100	5	50
Fig. 6	260	1–6	10	1.0, 1.5, 2.5	100	5	50
Fig. 7	260	4	6.5	2.0	100	5	0–55

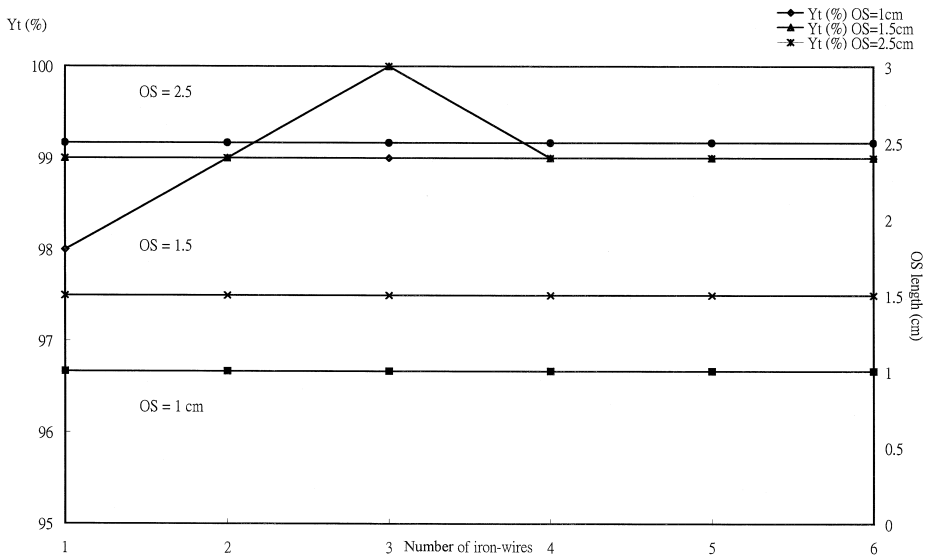


Fig. 4. Results of Cr-contaminated soil for a reactor size—100 ml with additives: IW and IS = 6.5 cm.

The efficiency of immobilization can be calculated by the following equations.

$$Y_t = [(C_s - C_o) / C_s] \times 100\% \tag{1}$$

$$I_t = [(C_o - C_t) / C_o] \times 100\% \tag{2}$$

Y_t is the non-leaching efficiency as a function of time; I_t is the efficiency of immobilization after t -minutes of treatment; C_s is original chromium-concentration

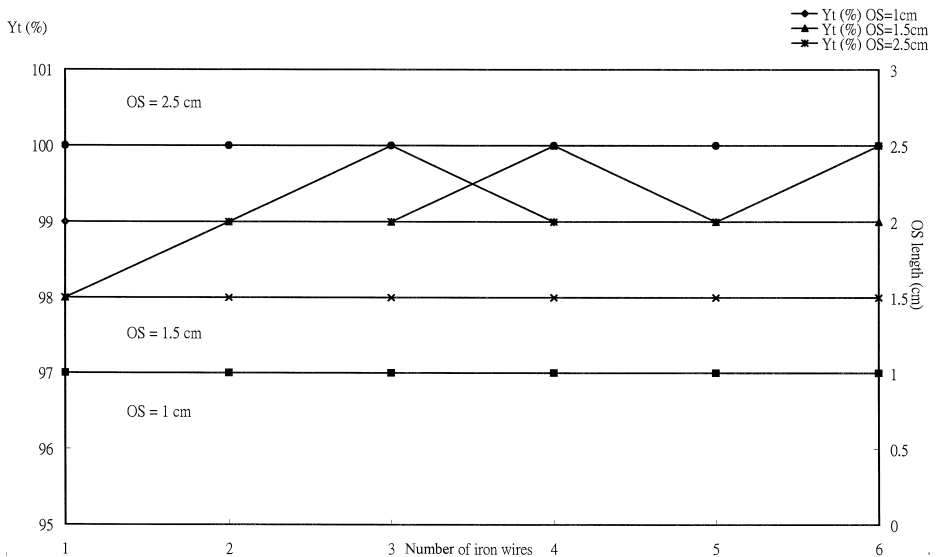


Fig. 5. Results of Cr-contaminated soil for a reactor size—100 ml with additives IW and IS = 7.5 cm.

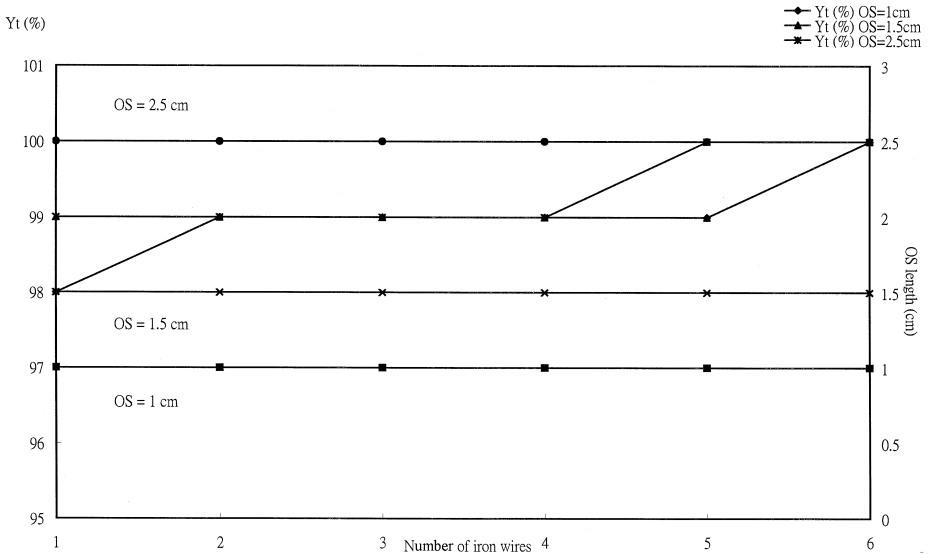


Fig. 6. Results of Cr-contaminated soil for a reactor size—100 ml with additives wires and IS = 10.0 cm.

(mg/l); C_0 is the leaching value before treatment; and C_t is the leaching value after t -minutes of treatment.

Results in Figs. 1–3 show GCF and SF parts with or without GAC. Figs. 1 and 2 differ in volume of the reactors (100 ml vs. 150 ml). In Figs. 1 and 2, low leachate values (less than 5.0 mg/l) were observed for C_s at initial concentration of 260 mg/l.

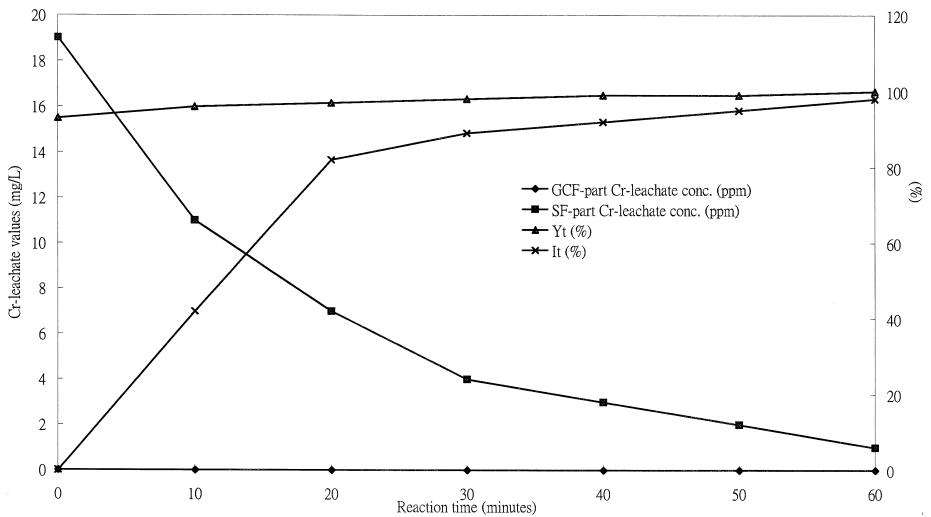


Fig. 7. Results of Cr-contaminated soil for a reactor size—100 ml with additives: four IW (IS = 6.5 cm and OS = 2.0 cm).

In the Fig. 1, the SF leachate values ranged from 1.8 to 3.2 mg/l, and also showed I_{50} greater than 90% at GAC height = 0.5 cm, and GAC: soil weight ratio = 0.43. Fig. 2 showed I_{50} greater than 90% at GAC height = 0.6 cm, and GAC: soil weight ratio = 0.04. The larger reactor-size (150 ml) yielded better Y_t and I_t than the one with smaller volume (100 ml). This suggests that the area exposed to MW field did affect the MW energy absorption. The energy absorption resulted in the higher immobilization rate of Cr.

Fig. 3 shows the results of vitrification of chromium-contaminated soil as a function of time. In Fig. 3, a vitrified GCF was first observed at $t = 15$ min; however, the SF has a leachate value = 8.0. Greater than 90% I_t was eventually observed when at t greater than (or equal to) 35 min. Fig. 3 demonstrates a large increase in Y_t and I_t between reaction time of 10 and 15 min. This suggests that the phenomenon of vitrification is a reliable indicator for an effective immobilization of Cr in soil. However, vitrification is not a requirement for Cr immobilization on soil, but it may not meet the USEP regulatory limit without vitrification. It means that SF can only provide a certain level of Cr immobilization.

In Figs. 4–6, all the GCF leachate values were less than 1.0 mg/l; all the SF leachate values were less than 4.8 mg/l. The vitrified depth of soil can reach about 7.0 cm with IS = 6.0 cm, 7.5 cm with IS = 7.0 cm, and 8.4 cm with IS = 10.0 cm.

In Fig. 7, GCF began to form at $t = 20$ min (IW-A03), however, with the SF leachate value was 7.0 mg/l. At $t = 30$ min, SF leachate value was 4.0 mg/l, but with $I_{30} = 87\%$. The reaction time must be greater than (or equal to) 40 min in order to achieve I_t greater than 90%.

The samples that used four IW as an additive in Figs. 4–7 showed break of penetration with three of the IW. A vitrification depth of 9.0 cm (Fig. 6, IS = 10 cm) showed that the IW were inducing a deeper penetration of the MW energy.

4. Conclusions

A MW radiation process that utilized GAC and IW to form a GCF has produced a relatively low Cr leachate values (less than 1.0 mg/l) for C_s at initial concentration of 260 mg/l. Although not all the non-vitrified parts (SF) can reach a leaching value less than 5.0 mg/l when the optimal condition was allowed, I_t greater than 90% can be achieved in less than 60 min. As the results indicated, the efficiency of this decontamination technology has been shown to be dependent on several factors, namely, C_s , time, surface area and the additive. This series of experiments have demonstrated that it is technically feasible to stabilize chromium in soil by the application of GAC or IW with MW radiation energy.

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