TESTING AND ANALYSES OF CHAT AND ASPHALT-CONTAINING
CHAT

Souhail R. Al-Abed, David J. Reisman, Gautham Jegadeesan, and Niranjan Deshpande

Abstract: Granular mine waste are generated from the extraction and beneficiation of lead/zinc minerals. The fine gravel waste, commonly known as chat, contains elevated levels of lead, zinc and cadmium which can result in potentially serious human health and ecological concerns. With the use of chat in a variety of applications such as road construction, there is an increased environmental concern due to the potential leachability of lead (Pb), cadmium (Cd) and zinc (Zn) at high concentrations. In this study, we examine the release of these three metals from raw chat and its reuse products, mainly cold-mix asphalt (CMA) and hot-mix asphalt (HMA), to determine the environmental stability of the materials under different environmental conditions.

The leachability of metals was evaluated using extraction tests including the toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP) and deionized water extraction procedure (DWE). In addition, the relative bioaccessibility of the metals was determined by the relative bioaccessibility leaching procedure (RBL) tests. Based on the conducted leaching tests, it was observed that all the three samples failed the TCLP test. The Cd and Pb concentrations in the TCLP extracts were higher than the mandated TCLP limits for leaching from wastes. The TCLP extracts of CMA and HMA samples were found to be less than the limit for Cd, but higher for Pb. The experimental data also showed that the concentrations of Cd and Pb in the SPLP extracts were less than the National Drinking Water Primary Standards of 0.005 mg/L and 0.015 mg/L, respectively. This indicated the suitability of the mine tailing and its reuse products for beneficial applications. The percent bioaccessible metal followed the order: raw chat < HMA < CMA, probably due to its smaller particle size (< 250 µm), compared to the particle sizes of CMA and HMA tested (< 2 mm). The data indicated that while the use of chat in asphalt is environmentally safe, care should be taken as metals could leach in significant concentrations when placed in moist environments for longer duration.

Additional Key Words: Mine waste, Lead, Cadmium, Leaching, Bioaccessibility, TCLP, SPLP

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INTRODUCTION

Granular mine wastes are generated from the extraction and beneficiation of lead/zinc minerals. For over one hundred years of activity ending in 1970, the Tri-State Mining District (Oklahoma, Kansas and Missouri) has been the source of a major share of the lead and zinc mined in the United States. Ore processing either by dry gravity separation or through a wet washing or flotation separation results in a fine gravel waste commonly called “chat.” (dry process) or tailings ponds used to dispose of waste material after ore separation (wet process). Surface piles of chat, as well as underground mining areas, extend uninterrupted across the Oklahoma - Kansas State line. Even though, most of the chat wastes have been removed, about 100 million tons of chat is presently stockpiled on the surface of these areas in large piles. In its bulk form, chat contains elevated levels of lead, zinc and cadmium that can result in potentially serious human health and ecological concerns through exposure (US EPA, 2007a; ODEQ, 2000, US EPA, 2007b).

Under the “Bevill Amendment of 1980”, chat is currently exempt from the Resource Conservation and Recovery Act (RCRA) Subtitle C regulation (US EPA, 1985, 2003, 2007a) because it is a mining waste. Under the new Chat rule issued by United States Environmental Protection Agency (US EPA), the Agency has concluded that chat used in hot-mix asphalt (HMA) or cold-mix asphalt (CMA) is safe and environmentally friendly. However, the rule is to be applied on a case-by-case basis and needs to meet US EPA’s criteria if: (1) the Synthetic Precipitation Leaching Procedure (SPLP) test (US EPA, 1997) extracts, provided in the SW-846 Manual (Method 1312) from the reuse materials such as HMA and CMA, have concentrations less than the National Primary Drinking Water standards (NPDW) and; (2) the metal release from chat used in any mixture is less than the NPDW standards (US EPA, 2007a; ODEQ, 2000, US EPA, 2007b).

Chat has been used in a variety of beneficial applications including: 1) applications that bind material into a durable product; these would include its use as an aggregate in batch plants preparing asphalt and concrete, 2) applications below paving on asphalt or concrete roads and parking lots, and 3) applications that use the material as a raw product for manufacturing a safe product. Environmental concerns on the use of chat in asphalt arise from metal leaching due to the elevated concentration of Pb, Cd and Zn. Evaluation of raw chat indicated that this waste in most unencapsulated uses has the potential to leach lead into the environment at levels which
may cause threats to humans (i.e. elevated blood lead concentrations in area children). Data reported in literature (Wasiuddin et al. 2005; Drake, 1999; US ACE, 2000) found SPLP results of milled (weathered) chat asphalt surface show did not exceed the primary drinking water standard for lead (0.015 mg/l) or cadmium (0.005 mg/l). The results also show that milled asphalt road bases and surfaces did not exceed the secondary drinking water standard for zinc (5 mg/l). Similarly, the use of chat in slurry seals, micro-surfacing, warm mix asphalt, cold mix asphalt, or epoxy seals were also found to be environmentally safe (Wasiuddin et al. 2005; Drake, 1999; US ACE, 2000). However, with the variations in metal content in chat across various locations and sampling depth, changes in leachability and bioaccessability can be expected. Bioaccessability is defined as the fraction of an administered dose that is soluble in the gastrointestinal environment and available for absorption. Research has indicated that in vivo animal studies and human exposure studies with parent minerals, such as galena, may have limited bioaccessability; nevertheless, with time, these primary minerals can suffer geochemical transformations that convert minerals from relatively refractory phases into phases with greater lability and bioavailability (Schneider et al., 2007; O'Day et al., 1998; Gasser et al., 1996). Exposure to moisture and oxygen allows oxidation of sulfide minerals such as galena, sphalerite, and chalcopyrite and leads to mineral dissolution and metal mobilization. Thus, it is important to evaluate the use of chat in asphalt on a case-by-case basis to determine the stability/leachability of the metals under different environmental conditions.

In this study, the release of metals (lead, zinc and cadmium) from raw chat and HMA and CMA using raw chat as the aggregate was examined. Since the SPLP tests adequately mimic leaching potential of solids when used in road construction, they will be used as screening tests. Additionally, the Toxicity Characteristic Leaching Procedure (TCLP) test was conducted, as it is a comparative measure of the leaching characteristics of chat and its mixtures. The bioaccessibility of metals was also determined in this study to determine the fraction of the metals that might be soluble and available for adsorption upon ingestion. The results obtained from the study will help to evaluate the potential hazards of the use of chat in asphalt.
MATERIALS AND METHODS

Sample Collection

The Elvin/Rivermines Mine Tailings site is one of the six major mine tailings sites in the Park Hills-Desloge-Bonne Terre area of St. Francois County, Missouri. The site is located between the former towns of Elvins and Rivermines, now part of the City of Park Hills. Mining activities commenced in the Old Lead Belt about 1890, with early operations including mining, milling, roasting, and smelting. In the early years, milling operations were conducted at numerous locations in the area. Milling operations were consolidated at Elvins around 1909. The Elvins Mill also processed ore from other area mines until it was permanently closed around 1940. The site consists of chat piles that cover approximately 0.08 km$^2$ and are approximately 51 m high, and a tailings area covering approximately 0.53 km$^2$. The tailings area is relatively flat and approximately 15 m lower than the chat pile (Fig. 1). "Chat" is a gravel-like waste product from mining and milling of lead ore, generally larger than 0.64 cm in diameter. "Tailings" are smaller, resulting from a different type of milling process. Tailings are generally less than 0.08 cm in diameter. Samples of raw chat were collected in 5 gallon buckets from the site (Fig. 1). Once collected, they were transported to the EPA Center Hill Facility in Cincinnati, OH. Upon receipt of the raw chat samples, the bucket was homogenized in rotary tumblers, rotating at 30 ± 2 rpm,

Figure 1. Location of the mine waste (chat) site. Panel A shows the piles of chat wastes at the site and Panel B shows the chat samples collected.
Asphalt samples were generated close to the chat waste site. Samples of CMA and HMA were collected by hand with a plastic scoop in 5 gallon buckets from the site. The CMA contained 100% of chat (by weight) and mixed with MC 800 oil at 111 °C. HMA contained 12-13% chat (as provided by sample collector), usually heated to 148 °C and compacted. CMA samples collected appeared to be granular and sticky (due to the oil base), while HMA appeared compacted, so it was crushed to generate granular samples for the experiments. To obtain appropriate particle size, the CMA and HMA samples were crushed to less than 2 mm sieve size using hammers. Since both the samples contained oil bases in them, they could not be homogenized in rotary tumblers due to agglomeration. Adequate amounts of the samples were crushed for the entire experiment.

**Characterization Tests**

The raw chat samples, HMA and CMA were subjected to acid digestion using the EPA Method 3051 in triplicate to determine “environmentally available” elements (US EPA, 1997). The National Institute of Standards and Technology (NIST) references, NIST 2709 and NIST 2710 were used as quality control. The moisture content of the samples was also determined using appropriate EPA methods (US EPA, 1997).

**Leaching Tests**

TCLP and SPLP extractions tests were conducted following US EPA protocols as stipulated in the SW-846 to determine metal mobility in landfill and land-applied scenarios (US EPA, 1997). All extractions were conducted at 20:1 liquid-to-solid ratio with a contact time of 18±2 hours in triplicate. In order to determine the relative bioaccessible amounts of metal in the solid samples, the samples were tumbled with the extraction fluid containing 0.4 M glycine and 5% HCl in deionized water for one hour at 37 °C (Drexler, 1998). The experiment was performed at 100:1 liquid-to-solid ratio with a contact time of 1 hour. The method specified the use of samples with particle size < 250 µm. Since CMA and HMA contained the oil base, they could not be sieved to less than < 250 µm. Therefore, samples (CMA and HMA) with less than 2mm particle sizes were used for the relative bioaccessibility test. On the other hand, the raw chat samples were sieved to less than 250 µm using US Sieve No 60 and used for the test. Additionally, the leaching of metals under groundwater conditions was evaluated by performing tests using deionized water as the extraction fluid. The test was similar to the TCLP and SPLP tests, albeit for 14 days.
Analytical Procedures

All extracts were decanted, filtered using 0.45 µm Nylon filters purchased from Whatman Inc., IL and acidified to pH <2. The metal concentrations were analyzed using an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, IRIS Intrepid, Thermo Electron Corporation, CA), in accordance with EPA Method 6010B (US EPA, 1997). All analytical data were assessed for accuracy and precision, strictly specified by EPA Method 6010B, including triplicate analysis, matrix spikes and method blanks. The detection limits for Pb was 14 µg/L, while that for Cd and Zn ranged from 4-5 µg/L. Metal recoveries from matrix spikes were within 80-120 % of the expected values.

RESULTS AND DISCUSSION

Characterization of Raw Chat, CMA and HMA

The moisture content in raw chat, cold-mix asphalt (CMA) and hot-mix asphalt (HMA) were observed to be very low. Averaging the percent moisture content among triplicate experiments indicated that the % moisture content was 1.66 % for raw chat, 0.79 % for CMA and 0.13 % for HMA. Table 1 provides the total metal content in raw chat, cold-mix asphalt (CMA) and hot-mix asphalt (HMA). As can be seen from the tabular data, the concentrations of Cd, Pb and Zn were highest in the raw chat samples. Comparing the CMA and HMA metal content, it can be observed that with the exception of Zn, both samples had the same metal concentrations (mg/kg). Previous research on multiple raw chat samples have shown that concentration of lead in the raw chat ranged from 210 mg/kg to 4,980 mg/kg, with an average of 1,461 mg/kg; cadmium ranged from 43.1 mg/kg to 199.0 mg/kg, with an average of 94.0 mg/kg; and zinc ranged from 10,200 mg/kg to 40,300 mg/kg, with an average of 23,790 mg/kg (Wasiuddin et al. 2005; Drake, 1999; US ACE, 2000). Upon comparison with earlier reported data, it can be seen that Pb concentration in raw chat was ~ 3 fold higher than the average value in this sample, ~ 10-fold lower for Zn and ~ 1.5-fold lower for Cd.
Table 1. Total metal content in raw chat, CMA and HMA

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Cd (mg/kg)</th>
<th>Co (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Fe (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Zn (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Chat</td>
<td>62.77</td>
<td>66.81</td>
<td>92.36</td>
<td>22145.51</td>
<td>36.72</td>
<td>5129.26</td>
<td>2891.64</td>
</tr>
<tr>
<td>Cold mix asphalt</td>
<td>49.17</td>
<td>31.32</td>
<td>57.13</td>
<td>20403.48</td>
<td>23.43</td>
<td>4295.80</td>
<td>1848.54</td>
</tr>
<tr>
<td>Hot Mix asphalt</td>
<td>33.95</td>
<td>30.89</td>
<td>80.75</td>
<td>15771.80</td>
<td>23.73</td>
<td>3989.09</td>
<td>827.16</td>
</tr>
</tbody>
</table>

TCLP leachable amounts

The results from the TCLP extraction tests are presented in Fig. 2. All samples failed the TCLP test according to concentration limits used in RCRA wastes. For the raw chat samples, the Cd concentration (1.1 mg/L) and Pb concentration (64.2 mg/L) were higher than the TCLP mandated limits of 1.0 and 5.0 mg/L, respectively. In the case of CMA and HMA samples, Cd concentrations were less than the TCLP mandated limit. However, Pb concentrations were 6-fold and 2-fold higher than the TCLP limits for CMA and HMA, respectively. As can be seen from the data, Zn concentration were also high, ranging from 57.7 mg/L in raw chat to 8.6 mg/L for HMA samples.

The results are in complete contrast to previously reported data in that the TCLP test extracted more metals from these samples, compared to those samples tested in other studies (Wasiuddin et al. 2005; Drake, 1999; US ACE, 2000). In a report published by the Oklahoma Department of Environmental Quality (OK DEQ) in May, 2000 (ODEQ, 2000, US EPA, 2007b), it was reported that TCLP values for raw chat samples showed lower concentrations of Pb (2.7-18.0 mg/L) and Cd (0.4-0.8 mg/L), compared to the data observed in this study. These data provide a basis for assuming that there is a high variation for metals among chat types. TCLP tests on the asphalt samples containing chat showed even lower Pb (0.05-0.2 mg/L) and Cd (0.01-0.02 mg/L) concentrations. Several hot mix asphalt samples were also tested in the Oklahoma University (OU) study using the TCLP test (Wasiuddin et al. 2005; Drake, 1999; US ACE, 2000). For surface samples, TCLP average concentrations for lead ranged from <0.01 mg/l to a high of 0.5 mg/l. TCLP average concentrations for Cd ranged from <0.01 mg/l to 0.2 mg/l and Zn concentration averages ranged from 11.3 mg/l to 28.5 mg/l. Road base samples usually have higher metals concentrations than do surface samples. For road base samples,
average TCLP Pb concentrations ranged from 0.07 mg/l to 2.0 mg/l, average TCLP Cd concentrations ranged from 0.01 mg/l to 0.09 mg/l, and average TCLP Zn concentrations ranged from 19.9 mg/l to 41.3 mg/l. The difference in the TCLP extract metal content can be attributed to the total availability of the metals in the solid samples and the ability of the acetate ions to extract the cationic metals (Cd, Pb and Zn). The data also confirms the need to determine the leachability of the metals on a case-by-case basis for appropriately evaluating their environmental stability.

Figure 2. TCLP test results on raw chat, CMA and HMA. (The TCLP limit mandated by RCRA is provided only for those elements listed, Cd and Pb. Zinc is not listed in the RCRA TCLP limits)

### SPLP leachable amounts

Table 2 presents the SPLP extract metal concentrations for raw chat, CMA and HMA samples. The SPLP limits reported in this paper are based on the Drinking Water Standards for Pb and Cd and the fresh water chronic National Recommended Ambient Water Quality Criterion
for zinc of 120 µg/l. As can be seen from the data, all samples passed the SPLP test and were lower than the limits. Most of the extract concentrations were below the instrument detection limits (IDLs) and the mandated SPLP limit, as regulated in the “chat rule”. The results obtained from previous studies also reported similar data (Wasiuddin et al. 2005; Drake, 1999; US ACE, 2000). Comparison of the SPLP results of milled (weathered) chat asphalt samples in the OU study with the National Primary and Secondary Drinking Water Standards, without dilution and attenuation, show that milled surface and road base mixtures did not exceed the primary drinking water standard for Pb (0.02 mg/l) or Cd (0.01 mg/l). The OU results also show that milled asphalt road bases and surfaces did not exceed the secondary drinking water standard for Zn (5 mg/l). The data suggested that chat mixed with asphalt can be used for construction of pavements and roads.

Table 2. SPLP test results on raw chat, CMA and HMA

<table>
<thead>
<tr>
<th>Analyte</th>
<th>SPLP Extract Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chat</td>
</tr>
<tr>
<td>Cd</td>
<td>0.003</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.010*</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;0.002*</td>
</tr>
</tbody>
</table>

N.A: Not applicable
* denotes the IDLs for the instrument used for analysis

Bioaccessible metal content

Relative bioaccessibility of a metal is used to determine the fraction of the contaminant in the solid sample that could be absorbed by an organism via a specific exposure route (Drexler, 1998). It should be noted that the relative bioaccessible test procedure requires the use of particle sizes less than 250 µm. While size fractionation of the raw chat samples was possible, it could not be performed for CMA and HMA samples. Thus, CMA and HMA samples passing through 2 mm sieves were used for the study.

The extraction data is provided in Table 3. The percent of bioaccessible metal was calculated as EL/TL x 100, where EL = extract metal (mg/kg) and TL = total metal (mg/kg) and also
provided in Table 3. As can be seen from the data, percent bioaccessible Pb was highest for raw chat samples (41.4 %), compared to the CMA (4.6 %) and HMA (6.7 %). Similarly, percent bioaccessible Cd and Zn was also higher for raw chat samples. In general, the percent bioaccessible metal followed the order: raw chat > HMA > CMA, indicating that encapsulation of the mine waste greatly reduced metal bioaccessability. Higher bioaccessible metal content in the raw chat sample suggested their environmental hazards and their need to be disposed in an appropriate manner.

Table 3. RBLP test results on raw chat, CMA and HMA

<table>
<thead>
<tr>
<th>Analyte</th>
<th>RBLP Extract Concentration (mg/L) (Percent bioaccessible metal (%))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chat</td>
</tr>
<tr>
<td>Cd</td>
<td>0.37 (58.5%)*</td>
</tr>
<tr>
<td>Pb</td>
<td>21.23 (41.4%)*</td>
</tr>
<tr>
<td>Zn</td>
<td>17.83 (61.7%)*</td>
</tr>
</tbody>
</table>

*Denotes the percent bioaccessible metal content

Deionized water extraction test

The deionized water test is performed to determine the leachability of metals from the samples using deionized water (DI) as the extraction fluid. The extract concentration was compared to the Drinking Water Standards for Pb (0.015 mg/L) and Cd (0.005 mg/L) and the fresh water chronic National Recommended Ambient Water Quality Criterion for Zn of 120 µg/l. As mentioned earlier, the pH of the extraction fluid added was not controlled. Figure 3 illustrates the Pb amounts leached from raw chat, CMA and HMA as a function of time. The concentrations of Cd and Zn were observed to be below the detection limit of the instrument. Most metals extracted from raw chat, CMA and HMA (with the exception of Pb) were less than the previously stated limits. As can be seen in Fig. 3, Pb extract concentrations from raw chat were observed to be higher than the EPA mandated limit. It was observed that the Pb leached higher initially, tapering to a steady value of ~ 0.15 mg/L over a duration of 14 days. In comparison, the leachability of Pb from CMA and HMA was almost 2-fold and 4-fold lower than that from raw chat, respectively. The higher amounts of Pb release may possibly be due to the
higher Pb content present on the surface of the unwashed chat samples. The presence of Pb on the surface of the solid is more readily available for dissolution, compared to a washed chat (from which fine fractions are removed). This could also explain the decrease in Pb concentration in the CMA and HMA extracts, which use sieved chat and are also encapsulated in an oil matrix. According to the extraction procedure, the data indicates that if raw chat and its use in asphalt were to come in contact with water, then the release (leaching) of Pb from the sample may be a cause of concern due to migration of the metal to nearby environments.

Figure 3. Pb extract concentrations in the deionized water extraction test.

CONCLUSION

This study details the evaluation of leaching of metals, specifically Pb, Cd and Zn from chat (mining waste) at one site and also from its beneficial reuse product, asphalt. The raw chat samples had higher metal concentration than their reuse product, CMA and HMA. The concentration of Pb (5129 mg/kg), and Zn (2891 mg/kg) in raw chat was a cause of concern.
With the exception of Zn and Cd, both CMA and HMA had similar metal concentrations, and they were much lower.

The leachability of metals was evaluated using the TCLP, SPLP and deionized water extraction procedure. Based on the leaching tests conducted, it was observed that all the three samples failed the TCLP test based upon usual waste mandated exceeded the limits based upon RCRA waste limits. The Cd and Pb concentrations in the TCLP extracts were higher than the mandated TCLP limits (SW-846 Method 1311), but chat is a Bevill-exempt waste and not subject to RCRA limits. The TCLP extracts of CMA and HMA samples were found to less than the limit for Cd, but higher for Pb. In comparison to other studies, some variance in the TCLP results was observed probably due to variance in the metal content of the chat waste. On the other hand, the three samples, chat, CMA and HMA passed the RCRA SPLP waste limits (SW-846 Method 1312). The experimental data showed that the concentrations of Cd and Pb were less than the National Drinking Water Primary Standards of 0.005 mg/L and 0.015 mg/L, respectively. In addition, the concentration of Zn in the SPLP extracts of the three samples were less than the fresh water chronic National Recommended Water Quality Criterion for zinc of 120 µg/L. The relative bioaccessability test showed that percent bioaccessible Pb was highest in the chat sample (41 %) and so was percent bioaccessible Cd (58 %). In general, the percent bioaccessible metal followed the order: raw chat < HMA < CMA, probably due to its smaller particle size (< 250 µm), compared to the particle sizes of CMA and HMA tested (< 2 mm). Deionized water extraction tests indicated that Pb could leach from raw chat in significant amounts (0.022-0.17 mg/L). Similarly, Pb concentration from HMA and CMA were also higher than the National Drinking Water Primary Standards of 0.015 mg/L. The concentrations of other metals were observed to be negligible. The results from the study suggested that, even though chat, CMA and HMA failed had higher metals in TCLP tests, they can be used for their current applications since they pass the SPLP tests, required under RCRA and EPA “chat rule” guidelines.

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**LITERATURE CITED**


