TREATMENT OF AUTO SHREDDER RESIDUE

Prepared for:

CALIFORNIA CHAPTER INSTITUTE OF SCRAP RECYCLING INDUSTRIES (ISRI)

Prepared by:

Mark J. Guatney, CHMM
Dir. of Environmental Services
Envirosure Solutions, LLC

George J. Trezek, Ph.D. Emeritus Professor Univ. of California, Berkeley

May 18, 2012

TABLE OF CONTENTS

I. BACKGROUND/HISTORY OF ISSUE	1
II. DESCRIPTION OF THE PROCESS THAT RESULTS IN THE GENERATION OF ASR	3
III. DESCRIPTION OF UNTREATED ASR	4
A. Physical Characteristics	5
B. CHEMICAL CHARACTERISTICS	5
C. Pre-Treatment Levels of Heavy Metals	6
IV. DESCRIPTION OF TREATMENT PROCESS	8
A. CHEMICALS, POZZOLANIC MATERIALS AND EQUIPMENT USED IN THE PROCESS	8
B. Soluble Silicate Solution	9
C. ALKALINE ACTIVATOR	9
D. EQUIPMENT AND PROCESS FOR TREATMENT	9
E. Treatment System Control and Calibration	10
V. CHEMISTRY OF TREATMENT PROCESS	12
A. METAL OXIDES TO METAL-SILICATES	12
B. CHEMICAL REACTION, NOT DILUTION	16
C. Influence of Particle Size	16
VI. LONG-TERM EFFECTIVENESS OF TREATMENT PROCESS	17
A. HISTORICAL ASR TREATABILITY STUDIES	19
B. RECENT ASR TREATABILITY STUDIES	22
VII. TREATED ASR – CHARACTERIZATION DATA REQUIRED BY LANDFILLS	26
A. LANDFILL LEACHATE TEST DATA	26
C. TREATED ASR CHARACTERIZATION DATA (TOTAL AND WET)	26
VIII. CONCLUSIONS	30
IV DEFEDENCES	21

Figures

Figure 1:	Process Flow Diagram of Auto Shredding and Separation Processes
Figure 2:	Formation of Liquid Silicate Polymer
Figure 3:	Polysilicate Reaction with Metallic Elements
Figure 4:	Portland Cement Reactions
Figure 5:	Log Graph of 3-Metal Concentration Using Multiple Extractions

Tables

Table 1:	STLC Metal Values in Untreated ASR
Table 2:	Long-Term Effectiveness Study Using Multiple Extractions
Table 3:	Historical ASR Treatability Data
Table 4:	Recent Treatability Data Using Belt-Collected ASR Samples
Table 5:	Comparison of Treatment Formulations
Table 6:	Summary of Landfill Leachate Testing of Treated ASR
Table 7:	Total and WET Results for Treated ASR

I. BACKGROUND/HISTORY OF ISSUE

Auto shredder residue (ASR) is generated by scrap metal shredding facilities as a result of the process of separating specification grade metal from a huge array of recyclable scrap metals including car bodies, household appliances, manufactured metal products and myriad other types of miscellaneous scrap metal. Since the mid- to late-1980s, shredder facilities in California have treated ASR using an in-line chemical fixation process to stabilize residual soluble metals prior to beneficial use or, less often, disposal of the treated material. The purpose of this Technical Memorandum is to explain how the treatment process is conducted, the types of materials and equipment that are used, the nature of the chemical reactions that occur in the process, and how these reactions bind residual heavy metals in the ASR so as to minimize their leaching potential over time. The vast majority of treated ASR is beneficially used as Alternative Daily Cover in nonhazardous waste landfills across the state, and is not subject to the more acidic environments that can be present in hazardous waste landfills. A survey of landfill leachate data conducted by the auto recycling industry in 2009, and submitted to the Department of Toxic Substances Control (DTSC), did not identify any instance where groundwater has been adversely affected by heavy metals in treated or untreated ASR deposited in those landfills.

The treatment process was developed in the mid-1980s in response to the classification of auto shredder residue as a California-only (non-RCRA) hazardous waste under the state hazardous waste regulations that were adopted by the Department of Health Services (DHS) (the predecessor agency to DTSC) in 1984. Prior to the adoption of those regulations, ASR was regulated as a nonhazardous solid waste and was disposed of in municipal landfills without treatment. DHS regulations established a variety of ways that wastes could be classified as hazardous wastes under California law, including the presence of heavy metals in concentrations that exceeded specified Total Threshold Limit Concentrations (TTLCs) or Soluble Threshold Limit Concentrations (STLCs), the latter as determined by the California Waste Extraction Test (WET). TTLCs and STLCs were adopted for a number of heavy metals commonly found in ASR, including lead, copper, cadmium and zinc.

Collectively, California metal shredder operations produce very large quantities of ASR (ranging from 500,000 to 700,000 tons per year). There are multiple obstacles (both regulatory and economic) to reducing this volume through waste minimization and recycling programs, e.g., regulatory impediments to recycling plastics. Shredder operators implement inbound material acceptance policies that require the rejection or removal of a wide variety of hazardous materials, hazardous wastes, and other "materials requiring special handling," as required by law or as necessary to ensure safe operations. This serves to minimize hazardous constituents in the ASR, but does little to reduce the overall volume. It was recognized by DHS that the costs associated with managing this very large volume of residual material as a hazardous waste were not

warranted based on the insignificant hazard posed by the material. At the same time, DHS recognized that the cost of managing ASR as hazardous waste would impose severe economic hardship on the shredder/recycling industry and alter the economics of the industry in a way that could destroy its viability. Aside from loss of jobs, loss of the industry in California would lead to the improper handling of discarded vehicles, old appliances and other scrap metal, to the detriment of public health and safety and the environment. Thus, development of an effective inline treatment process was seen as a means to allow ASR to continue to be managed as a nonhazardous waste and to maintain the viability of metal recycling for the benefit of the public.

Following implementation of the treatment process, the shredder operators applied for reclassification of the treated ASR as non-hazardous waste under then § 66305(e) of the Title 22 regulations (since recodified as § 66260.200(f)), on the grounds that the waste possessed mitigating physical and chemical characteristics that rendered it insignificant as a hazard to human health and the environment. Each application was supported by analytical data that compared the solubility of key heavy metals (primarily lead and cadmium) in the waste before and after treatment. Each of the applications for reclassification was granted based on the demonstrated effectiveness of the treatment process. These reclassification letters have set the standard for ASR treatment and beneficial reuse for over 25 years.

DTSC has requested preparation of a Technical Memorandum on the ASR treatment process in connection with its review of the regulatory status of treated ASR and consideration of possible alternative management standards for treated ASR. DTSC's evaluation of the long-term effectiveness of the treatment process, and the use of treated ASR as alternative daily cover in nonhazardous waste landfills, is a critical component of this regulatory strategy.

II. DESCRIPTION OF THE PROCESS THAT RESULTS IN THE GENERATION OF ASR

ASR is generated during the recycling of end-of-life manufactured "light iron" products such as automobiles and household appliances, as well as a huge variety of other types of recyclable scrap metal (ISRI, 2011). The term "auto shredder" comes from the initial step in the recycling process in which the recyclable material feedstock (frequently containing flattened car bodies) is placed by material handler or conveyed into a large hammermill shredder to reduce the size of the scrap metal into smaller pieces that can be more easily handled and separated by material type into specification-grade scrap metal commodities. Although the term ASR implies a dedicated in-feed of scrap automobiles, ISRI has estimated that as much as 40% of ASR derives from end-of-life appliances (Hook, 2008). In the second step of the recycling process, large electromagnets are used to separate most of the ferrous metal (e.g., steel) from the nonferrous metals (e.g., copper, aluminum and stainless steel) and other non-metallic materials contained in the shredder output ("aggregate").

Once the ferrous metal (or "shred") has been separated from the shredder aggregate, trommels and other kinds of "downstream" separation equipment are used to separate and size the remaining materials into different fractions so that they can be further processed to optimize removal of valuable metals. These fractions can be based on weight, density or other readily distinguishable physical properties. Specification-grade nonferrous metal is typically separated from the non-metallic material by eddy current separators (which create a means for magnetic separation of the nonferrous metals) and, more recently, by more advanced mechanical separation methods (e.g., optical sortation). Other types of specialized equipment may be used to sort the nonferrous metals and other materials into a variety of recyclable commodities. Depending on the sophistication of the material separation stages that are employed, the recyclable materials can be size-sorted and density-sorted onto separate conveyor belts to improve the recovery rate of different types of nonferrous metals and other recyclable commodities. In addition, manual labor may be used along certain conveyor belts to hand-separate larger pieces of nonferrous metals, and additional magnets may also be positioned to separate out remaining ferrous metals.

The largely non-metallic material remaining after the various magnetic, mechanical and manual separation steps is referred to as ASR. The ASR is treated by the process described in this paper, which includes final screening by a magnet installed downstream of the treatment process to collect any remaining ferrous metal after the in-line treatment process.

A flow chart depicting a typical auto shredding and "downstream" material separation processes is presented in Figure 1.

Shredder In-feed **End Products** Hammermill Shredder **Ferrous** Oversize **Fraction** Magnet Ferrous Metal Return to Z-Box Separation Product Shredder Non-Ferrous Fractions Non-Ferrous Metal **Products** Auto Shredder Separation Residue (ASR) Mixing Stage 1 Mixing Stage 2 **ASR Treatment Pug Mill** Treated ASR Final Magnet Alternative Daily Cover

Figure 1: Process Flow Diagram of Auto Shredding and Separation Processes

III. DESCRIPTION OF UNTREATED ASR

The Vehicle Recycling Partnership, LLC (VRP) estimates that up to 84% (by weight) of a shredded automobile is separated into specification-grade metals by the scrap recycling industry (Metal Bulletin Daily, 2008). USEPA estimates are slightly more conservative at 75% to 80% (USEPA, 2011a). The remaining 16% to 25% of the recycled automobile becomes ASR. Current estimates suggest that more than 5 million tons of ASR is produced in the U.S. each year, and nearly all of this is used as Alternative Daily Cover or landfilled as waste (USEPA, 2011a). California is one of the few states that require treatment of ASR prior to placement in a solid waste landfill for either disposal or use as Alternative Daily Cover.

While generally homogeneous and soil-like in overall appearance, ASR is actually a highly heterogeneous mix of material which typically includes plastics, rubber, foam, fabric, carpet, glass, wood, road dirt, and debris, along with a small amount of residual (primarily nonferrous) metal that was not removed by the prior separation processes. These materials make up a complex mix of sizes, shapes, and densities with physical and chemical properties as described in Subsections A and B below. As noted by USEPA (2011a), research on ASR composition by Hook (2008) and DeGaspari (1999) determined that plastics represent approximately 30% of ASR's weight. Foam represents approximately 5% by weight, but up to 30% of the volume of ASR.

A. Physical Characteristics

The physical characteristics of ASR range from granular particles (e.g., sand and soil) to identifiable pieces of carpeting, wood, foam, or plastic sometimes exceeding 5 inches in cross section. While, historically, California shredders treated only the smaller fractions of ASR (which were referred to as "fines"), the treatment process has evolved over time so that now all but the largest fraction of materials contained in ASR (plus 4-inches) is treated. The plus 4-inch materials are typically returned to the shredder for re-processing.

B. CHEMICAL CHARACTERISTICS

The chemical characteristics of ASR are typified by the presence of a very small amount of residual metals, such as lead, cadmium, copper and zinc, as well as various petroleum hydrocarbons (e.g., lubricating oils and other residual automotive fluids) and PCBs. Concentrations of certain residual metals in untreated ASR can approach or exceed California TTLCs and STLCs. For example, untreated ASR often contains total lead in excess of 1,000 mg/kg and WET extractable lead in excess of 5 mg/l. These constituents are also detected in samples of treated ASR collected by the shredders to comply with the requirements of the receiving landfills, although the extractable concentrations of metals are significantly reduced as

a result of the treatment process. Concentrations of petroleum hydrocarbons, PCBs, VOCs and SVOCs are typically far below levels that would cause ASR to be classified as hazardous based on these constituents.

The residual metals found in ASR are constituents of the raw (unprocessed) scrap originally fed into the shredder. The limited chemical characteristics of untreated ASR reflect the significant efforts of the shredder facilities and their upstream suppliers to keep hazardous materials out of shredder feedstock in the first instance. Each auto shredder facility implements an inbound material acceptance policy that prohibits the inclusion of a range of hazardous materials in the shredder in-feed material. Each facility engages in stringent practices to enforce these prohibitions, including gate inspections of incoming loads of scrap by trained inspectors to identify prohibited materials in the incoming loads and vard inspections at various points en route to and at the entrance to the shredding process. Facilities also participate in the statemandated programs to require suppliers to remove "materials requiring special handling" from automobiles and appliances prior to crushing and delivery to the facility, and to remove mercury switches, batteries and other hazardous materials from scrap auto bodies. Automotive fluids (fuels, lubricating oils, transmission fluid, antifreeze, etc.) are also drained from the vehicles prior to crushing and delivery to the shredder facility. In some cases, vehicles and appliances are received directly at the shredder facilities without having been prepared for recycling by an auto dismantler or a certified appliance recycler. Procedures are in place at the shredder facilities to remove all prohibited materials from these vehicles and appliances before they are shredded. Each of the shredder facilities reviewed for this report is a certified auto dismantler and appliance recycler.

C. Pre-Treatment Levels of Heavy Metals

Examples of recent WET extractable metal data from untreated ASR are provided in Table 1.

Table 1
WET Metal Values in Untreated ASR (mg/L)

Sample Date	Cd	Pb	Zn	Cu
6/18/2009	0.086	58.7	925	1.25
7/28/2009	1.29	41.8	1320	2.66
8/21/2009	0.657	88.3	1423	0.426
11/12/2009	1.25	49.6	1456	5.98
5/19/2010	2.57	155	864	6.83
10/26/2010	2.09	109	2603	9.1
1/5/2011	1.62	86.7	1685	3.97
1/25/2011	0.64	74.4	1025	3.35
4/28/2011	1.26	68.9	1110	4.51
10/31/2011	1.86	29.4	1970	4.60
11/7/2011	1.79	51.0	1525	2.03
Regulatory Values (CCR, Title 22 Ch. 11, § 66261.24)	1	50*	250	25

Bold numbers indicate values at or above the STLC value.

^{*} Each of the reclassification letters issued to the shredders allows a soluble lead concentration of 50 mg/L. The requirements of the reclassification letters vary with respect to other Title 22 metals.

IV. DESCRIPTION OF TREATMENT PROCESS

The treatment process at the three auto shredder facilities reviewed for this Technical Memorandum involves a chemical reaction between the ASR and inorganic binders that results in the binding and fixation of heavy metals in the ASR, thus reducing their leaching potential.

Treatment processes that chemically bind heavy metals in a solid or semi-solid matrix are referred to by USEPA as Stabilization treatment. Stabilization has been shown to be effective for a wide range of constituents including lead, arsenic, and chromium (USEPA, 2009). Stabilization and a similar process called Solidification are common remediation technologies employed at state and federal Superfund sites. USEPA estimates that 23% of the source control remedies performed at these sites between 1982 and 2005 involved the use of solidification or stabilization, and 94% of the solidification/stabilization remediations performed included inorganic binders such as cement, fly ash, lime, phosphate, soluble silicates, or sulfur (USEPA, 2009). The treatment technologies and terms Stabilization and Solidification were originally described in USEPA's "Guide to the Disposal of Chemically Stabilized and Solidified Waste" (USEPA, 1980). Unlike Solidification, which requires a substantial amount of cement or other inorganic binder to form a solid mass of material, Stabilization relies on reducing the contaminants' mobility through physical or chemical reactions involving precipitation, complexation, and adsorption (USEPA, 2006). The usefulness of this approach for stabilizing lead-impacted soil is described in the peer-reviewed Emerging Technologies for the Remediation of Metals in Soils by Interstate Technology and Regulatory Cooperation Working Group (ITRC, 1997).

The specific technology used to chemically bind the metals in the ASR matrix consists of the application of a blend of liquid polysilicates and additives (usually wetting agents), followed by the addition of an inorganic binder and alkaline activator (AA) such as cement, lime, or other pozzolanic materials. Depending upon the supplier, various types of silicate blends, using either potassium or sodium silicate with proprietary additives, are available and used by the auto shredding industry. Despite the variations in proprietary blends, the same basic principles of chemical reaction apply in each case.

A. CHEMICALS, POZZOLANIC MATERIALS AND EQUIPMENT USED IN THE PROCESS

The ASR treatment process, as currently conducted, uses one of two proprietary, soluble polysilicate solutions (with potassium silicate or sodium silicate as the active ingredient), and a form of pozzolanic (cementitious) material which functions as an alkaline activator (AA) in the process. The following sections discuss these liquid and dry additives, along with the process equipment necessary to deliver the treatment technology. Different treatment chemicals are

evaluated from time to time, and may be used in lieu of the chemicals described in this report if determined to be more cost-effective.

B. SOLUBLE SILICATE SOLUTION

Two of the three auto shredder facilities in California that treat their ASR use a commercially-available product known as Metbond MCX-90, manufactured by Envirokem Engineering Services, LLC of Stockton, California. The active ingredient in Metbond MCX-90 is sodium silicate complex, with pH in the 10+ range (i.e., non-concentrate) (Envirokem, 2008). The Metbond MCX-90 system employs mixing tanks and a chemical-to-water mix ratio of 3% to 20% by weight, depending on the moisture content of the ASR.

The third auto shredder facility uses a product known as HP Treatment, which is manufactured by C.C.I. Chemical Corporation (formerly Cherokee Chemical), with corporate offices in Vernon, California (C.C.I., 2011). The active ingredient in HP Treatment is potassium silicate, with a pH of approximately 11.2. This product was developed by C.C.I. and the auto shredder client and includes a single-user proprietary blend. The HP Treatment system employs an inline mixing process, and water-to-chemical mix ratio of approximately 13 to 1.

In addition to the water that is added to the polysilicate solution prior to application to ASR, the ASR itself is wetted during the shredding and separation stages, and it enters the treatment system with an average moisture content between 15% and 30% by weight.

C. ALKALINE ACTIVATOR

The California auto shredder facilities that treat ASR use Portland cement, fly ash, lime or similar dry pozzolanic material as the alkaline activator (AA). Based on the MSDS sheet for Portland Cement manufactured by CEMEX, of Victorville, California, Portland Cement has a pH in water of 12 +, and a specific gravity of 3.15 (CEMEX, 2001). Calcium salts in the blend may include: 2CaO.SiO₂, 3CaO.Al₂O₂, 4CaO.Al₂O₃Fe₂O₃, and CaSO₄.2H₂O. Small quantities of other salts such as MgO, K₂SO₄, and Na₂SO₄ may also be included (CEMEX, 2001).

D. EQUIPMENT AND PROCESS FOR TREATMENT

Although the actual equipment may vary at different shredding facilities, the basic approach for delivering the silicate treatment is very similar. A brief description of the equipment and process follows.

The first step in the process is to thoroughly wet the material requiring treatment with the silicate blend. This is accomplished by creating a silicate/water mixture and applying it to the untreated ASR. Typically, this mixture is delivered through sprays which impinge on the material as it

leaves the downstream nonferrous separation system conveyor belt. In some cases a two-compartment tank is used to create the silicate/water mixture. Here, the concentrated silicate blend from one compartment is metered along with water into a second compartment and is then pumped to a series of spray nozzles. In this case, the water acts as the carrier for the silicate blend so that the ASR can be wetted, thereby ensuring the even distribution of silicates throughout the material.

The amount of silicate necessary to effectively treat the ASR has been established through treatability studies conducted in the past, and is added in proportion to the amount of material requiring treatment. For example, if 40 tons/hour of ASR requires treatment and the appropriate silicate addition is 0.5 gallons/ton, then 20 gallons/hour of silicate concentrate would be added to the mixing tank. The amount of water/silicate mixture sprayed from the mixing tank has been determined through experience to be sufficient to ensure thorough treatment of the material. Since the water content of the in-feed to the treatment system varies (mainly due to the amount of water added in the shredder), the spray rate is adjustable to avoid free-liquid or oversaturation of the ASR. However, the amount of silicate that is added does not change.

Another method of silicate addition involves the use of a foam in-line jet pump mixer. In this application, the concentrated silicate blend is drawn from a silicate concentrate container by a combination of pressurized water and compressor airflow and sprayed onto the ASR as it falls off the end of a discharge conveyor. Adjustments can be made to the flow rates of water and silicate blend in this system, but typically the flow rate is set for the maximum feed rate of ASR on the belt.

The addition of the alkaline activator (AA) is the final step in the treatment process. After the ASR has been wetted with silicate/water solution, it enters a pug mill mixer. After an appropriate residence time in the mixer, the dry AA is introduced into the pug mill from an intermediate storage hopper, pneumatically connected to a large storage silo, via a set of variable speed metering screws. At some facilities the AA is metered directly from the silo, and multiple silos are used. The amount of AA required is a function of the known (predictable) range of concentrations of metals typically present in ASR and type of AA in use. Each system reviewed for this report included a computer-controlled metering of the AA, based on the conveyor belt weight of the ASR to be treated.

E. TREATMENT SYSTEM CONTROL AND CALIBRATION

Sampling and analysis over time has shown that shredder facilities process a relatively consistent mix of scrap, auto bodies and "tin" such that the levels of metals in shredder residue tend to remain within a relatively narrow range or band of concentrations. The treatment levels are conservatively adjusted to the higher end of the range.

Treatment of ASR May 2012

The treatment process has also evolved over time, with an eye towards optimizing the process and allowing use of different, more effective or more economical treatment chemicals. Periodic sampling of the treated ASR is also used to adjust the ratios of silicates and AA to achieve the reductions in extractable metals in the treated ASR, as necessary to comply with applicable Waste Discharge Requirements of the receiving landfills or the conditions, if any, of the facilities' reclassification letters. The treatment systems are designed so that adjustments can be made to the amount of wet or dry chemicals required.

V. CHEMISTRY OF TREATMENT PROCESS

The following section describes the chemistry involved in the ASR treatment process.

A. METAL OXIDES TO METAL-SILICATES

The metals in ASR are typically present in the oxide form. Due to the strong affinity of silicates for metallic/metal oxide compounds, these metals react with the silicates, resulting in the production of compounds referred to as metal-silicates. The chemistry of the process requires two components for the development of metal-silicates. The first is a soluble reactive silicate complex and the second is the AA which creates a high alkalinity environment to enhance the dissolution reaction of the metallic particles in the ASR. The reactive silicate is formulated to react with the available metals to create the insoluble metal-silicates. The metal speciation determines the metal-silicate solubility and required dose for treatment. Furthermore, the reactive silicate is formulated to inhibit the formation of metal hydroxides. The process is a water base reaction where both reagents are thoroughly mixed with the ASR.

A detailed description of the chemical reaction equations is given in "Remediation of Heavy Metal Contaminated Solids Using Polysilicates," (Trezek, 1994). Example chemical equations involved in formation of liquid silicate polymer, its fixation to metallic elements, and Portland cement reaction are repeated in Figures 2 through 4.

Figure 2: Formation of Liquid Silicate Polymer

Water

$$2 H_2O \leftrightarrow H_3O^+ + OH^-$$

Liquid Silicate

As noted above, the liquid silicates depolymerize when mixed with water, and thereby expose their negatively charged oxygen sites. Silicone backbones continue to break down in water, creating ionically charged clusters.

Figure 3: Polysilicate Reaction with Metallic Elements

When ASR with active metallic elements is introduced, the reaction can be characterized as follows:

The evidence of structural changes in treated materials has been recorded through the application of electron microscopy and X-ray diffraction studies conducted at the Eitle Institute of Silicate Science under the direction of Professor William Kneller (Krofchak, 1979). These studies and analysis identified the presence of silicate compounds in a comparison of before and after treated material. For more information on these microscopic studies of the silicate reactions, please refer to the Krofchak reference included in Section IX.

Once the polysilicate solution has been added and thoroughly mixed with the ASR, a dry AA such as Portland cement is added to the partially-treated ASR in the pug mill. The addition of Portland cement to the treatment process yields the following reactions:

Figure 4: Portland Cement Reactions (in cement chemistry notation)

$$2C_3 \cdot S + 6H \rightarrow 3C \cdot 2S \cdot 3H + 3(CH)$$

 $2C_2 \cdot S + 4H \rightarrow 3C \cdot 2S \cdot 3H + CH$
 $4C \cdot A \cdot F + 10H + 2(CH) \rightarrow 6C \cdot A \cdot F \cdot 12H$
 $3C \cdot A + 12H + CH \rightarrow 3C \cdot A \cdot CH \cdot 12H$
 $3C \cdot A + 10H + C\overline{S} \cdot 2H \rightarrow 3C \cdot A \cdot C\overline{S} \cdot 12H$

Where: C = CaO, $S = SiO_2$, $H = H_2O$, $A = Al_2O_3$, $F = Fe_2O_3$, $C\overline{S} = CaSO_4$, (USEPA, 2008, p. A-3).

Although, at the time this report was prepared, each of the auto shredders reviewed for this report was using Portland cement as its AA additive, similar reactions and results can be achieved by using other pozzolanic AA additives.

The underlying principle of the technology is the transformation of the metal oxides into insoluble metal-silicates. Thus, it is the silicates that are the primary treatment chemical, with the AA in the supporting role of pH adjuster. The solubility curves of the primary metals of concern, such as lead, cadmium, zinc, have parabolic shapes with the lowest solubility inflection points falling within a range of approximately 9.5 to 11 on the pH scale (Cullinane, Jones & Malone, 1986). It is the behavior of these curves that controls the optimum amount of AA addition. For example, if a five percent addition gives good results, doubling the amount to ten percent will not be twice as effective. Instead, this action would result in a shift to a higher part of the solubility curve or a higher solubility constant. Controlling the amount of AA addition is part of the ongoing monitoring process, and is necessary to maximize treatment efficiency and minimize the cost of treatment additives and the incremental increase in the weight of the treated ASR.

B. CHEMICAL REACTION, NOT DILUTION

Dilution is not a factor in this treatment process, as seen by a simple mass balance of metal solubility and treated ASR weight increases. If the addition of silicates and AA increase the overall treated weight of ASR by 5% to 10%, then simple dilution would decrease the soluble metal concentrations by a similar amount. However, test results show that reductions in metal solubility are in the range of 67% to 99% for the primary metals of concern in ASR samples (Cd, Pb and Zn). See Table 3.

It should also be noted that the silicate treatment is designed to reduce only metal leachability or solubility. This treatment does not alter the total concentration of metals in the ASR beyond the modest decline associated with an increase in weight due to the addition of 5% to 10% cement or other AA.

C. INFLUENCE OF PARTICLE SIZE

The reduction of metals leachability in the ASR is caused by the chemical reactions previously described, as well as by the increase in small particle size attributed to the adsorption of silicate followed by the AA binder. The addition of silicates reduces the time required for curing of the cementitious AA binder, and increases its hardness and resistance to acid attack (PQ® Corp, 2011). This effect was studied by Davis, Krumrine, Boyce and Falcone in the mid-1980s. Their experiments determined that the time required for a highly acidic solution to leach away 50% of a 2 cm particle size can be increased 100-fold by the addition of soluble silicates (Davis, Krumrine, Boyce, and Falcone, 1986). Experiments by Dr. Trezek in the 1980s also confirmed that this significant reduction in metals leachability is even more pronounced in smaller particles, when exposed to multiple simulated landfill leachate extractions using either of two dilute acidic solutions (Trezek, 1994). These experiments and others, along with the known characteristic of cementitious materials to continue to harden for years after initial reaction, confirm that the effectiveness of the treatment will continue after the ASR is placed in the landfill environment. The long-term effectiveness of the treatment process is discussed in Section VI.

VI. LONG-TERM EFFECTIVENESS OF TREATMENT PROCESS

As part of the early development of the polysilicate treatment technology in the late 1980s, Dr. Trezek studied the effect of metals leachability during successive extractions on identical samples of treated and untreated soil media (Trezek, 1994). In order to evaluate the durability or time-dependent stability of treated material, USEPA developed the Multiple Extraction Procedure (MEP) as a test method. The details of this procedure are described in SW-846, Method 1320 (USEPA, 1986). The California Waste Extraction Test (WET) and the Multiple Extraction Procedure were applied sequentially to soil contaminated with copper, lead, and zinc.

This treatability study included one initial extraction by the California WET method and nine additional extractions of the same sample by EPA Method 1320. The results of the initial WET on the untreated soil yielded extractable metal concentrations of 22 mg/l for copper, 110 mg/l for lead, and 106 mg/l for zinc (a total of 238 mg/l for all three metals) (Trezek, 1994). Comparisons between the treated and untreated samples, and subsequent extraction results, were performed using the extractable total of all three metals. Results of these multiple extraction tests are tabulated below, and graphed in Figure 5, which follows.

Table 2
Long-Term Effectiveness Study Using Multiple Extractions

Extraction/Method	Untreated 3-Metal Conc. (mg/l)	Treated 3-Metal Conc. (mg/l)	Reduction in Conc. of Extractable Metals (Treated vs. Untreated)	Percent Reduction from Prior Treated Extraction
#1 / WET Method	238	11.7	95%	NA
#2 / Method 1320	2.5	0.7	72%	94%
#3 / Method 1320	0.65	0.03	95%	96%
#4 / Method 1320	0.03	0.03	0%	0%
#5 / Method 1320	0.06	0.03	50%	0%
#6 / Method 1320	0.18	0.03	83%	0%
#7 / Method 1320	0.13	0.03	77%	0%
#8 / Method 1320	0.11	0.03	73%	0%
#9 / Method 1320	0.11	0.03	73%	0%
#10 / Method 1320	0.09	0.03	67%	0%

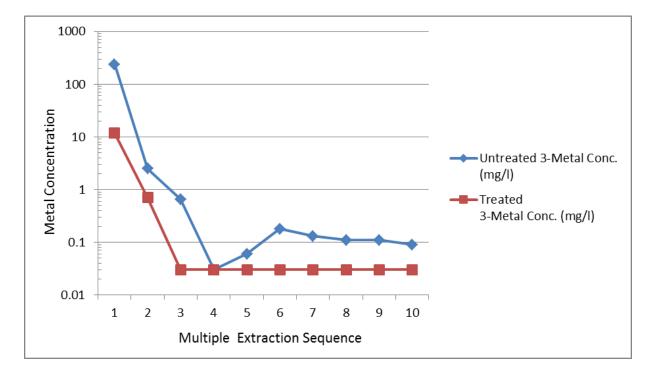


Figure 5 Log Graph of 3-Metal Concentration Using Multiple Extractions

As noted in Table 2, extractable target metals present in the untreated sample were reduced by 95% using polysilicate/cement treatment, as evidenced by the first extraction of treated and untreated samples using the WET method. The comparison of initial WET extractions of untreated and treated samples is also graphically depicted above as extraction #1.

Subsequent extractions by EPA Method 1320 (extractions 2 thru 10 on the graph) showed a decline in extractable metals in the treated sample over the next two extractions (94% and 96%, respectively), then reached the equilibrium extractable value (0.03 mg/l) for the remainder of the extraction tests. The untreated sample required four extractions to reach the same extractable metal concentration observed in the third extraction of the treated sample, and then rebounded to a higher concentration in the remaining extraction tests. This long-term effectiveness study demonstrates that treatment by polysilicate solution and alkaline additive reduces the WET-extractable metals concentration in soils by an average of 95%, and that this treatment benefit is durable enough to withstand multiple extractions (by Method 1320).

It should be noted that the Multiple Extraction Procedure (MEP) is designed to simulate 1,000 years of freeze and thaw cycles and prolonged exposure to an acidic environment (USEPA, 2003). The MEP also gradually removes excess alkalinity from the sampled material, thereby decreasing the pH and ultimately increasing the solubility of most metals. This pH reduction is significant because of the alkaline activator employed in the treatment system and the metals

solubility curves previously discussed, and further validates that the treatment has long-term effectiveness, even in an acidic environment.

Although this study used soil as the treated media, similar long-term effectiveness can be expected in soil-like ASR, as evidenced by the treatability studies and empirical data for treated ASR, which are discussed in the following sections.

A. HISTORICAL ASR TREATABILITY STUDIES

Dr. Trezek has been performing treatability studies on ASR since the late 1980s, and the following tables provide treatability data from his initial work, as well as more recent studies by Dr. Trezek and others.

Historical total (mg/kg) and extractable (mg/l) metal concentrations, as determined by the California WET method, for California shredder facilities are provided in Table 3 below. These data, which are from the 1988-1989 time period, were collected as part of the original ASR treatability studies conducted by Dr. Trezek. These data were generated for the purpose of demonstrating the effectiveness of the polysilicate/cement treatment in substantially reducing the extractability of metals found in ASR. Table 3 features cadmium (Cd), lead (Pb) and zinc (Zn), as these were the primary metals of concern to DTSC.

Table 3
Historical ASR Treatability Data

SAMPLE	SAMPLE TYPE	TYPE OF		ET results in mg/ stal results in mg/	
DATE	ITPE	ANALYSIS	Cd	Pb	Zn
	Untreated	WET	2.9	65	950
3/17/1988	onereacea	Totals	76	2900	14000
3/17/1988	Treated	WET	0.14	39	140
	rreaced	Totals	35	2800	6500
	Untreated	WET	2.60.	73	780
3/18/1988		Totals	52	2400	12000
3/18/1988	Treated	WET	0.17	16	23
		Totals	37	1800	7400
	Untreated	WET	2.4	93	570
3/19/1988	onci eaced	Totals	56	2400	9800
3/19/1988	Treated	WET	0.26	7.1	12
	Heateu	Totals	30	1500	5700

Table 3 - Historical ASR Treatability Data (continued)

SAMPLE	SAMPLE	TYPE OF	WET results in mg/L Total results in mg/kg			
DATE	TYPE	ANALYSIS	Cd	Pb	Zn	
	Untreated	WET	1.8	73	530	
3/22/1988	oncreaced	Totals	54	3200	11000	
3/22/1300	Treated	WET	0.2	19	53	
	rreaced	Totals	50	2800	7900	
	Untreated	WET	1.4	48	440	
3/25/1988	oncreaced	Totals	20	970	5100	
3/23/1988	Treated	WET	0.11	19	110	
	rreaced	Totals	17	1500	4100	
	Untreated	WET	1.8	65	67	
3/29/1988	Uncreaced	Totals	100	1900	8500	
3/29/1988	Treated	WET	0.85	19	160	
	rreated	Totals	90	1900	5900	
	Untreated	WET	0.75	34	180	
4/1/1988		Totals	26	1000	6500	
4/1/1900	Treated	WET	0.48	31	82	
		Totals	18	1200	5500	
	Untreated	WET	0.45	24	150	
4/5/1988	Uncreaced	Totals	35	1100	8300	
4/3/1988	Treated	WET	0.6	25	140	
	rreaceu	Totals	20	650	5100	
	Untreated	WET	0.8	31	260	
4 /0 /1000	Uncreaced	Totals	29	1300	9000	
4/8/1988	Treated	WET	0.25	5.5	12	
	rreateu	Totals	18	1700	7700	
	Untreated	WET	0.78	36	240	
1/12/1000	onci eaceu	Totals	17	660	3100	
4/12/1988	Treated	WET	0.05	6.4	7.6	
	rreaceu	Totals	22	1200	4600	

Table 3 - Historical ASR Treatability Data (continued)

SAMPLE	SAMPLE	TYPE OF		ET results in mg/L otal results in mg/kg		
DATE	TYPE	ANALYSIS	Cd	Pb	Zn	
	Untropted	WET	0.59	25	450	
A /1E /1000	Untreated	Totals	20	1000	5700	
4/15/1988	Treated	WET	0.03	3.5	12	
	rreaceu	Totals	20	650	3800	
	Untreated	WET	1.5	30	590	
4/19/1988	onci eaced	Totals	21	790	6800	
4/19/1988	Treated	WET	0.06	5.8	30	
	rreaced	Totals	25	1000	5700	
	Untreated	WET	1.1	47	480	
4/22/1988	Uncreaced	Totals	35	3900	9400	
4/22/1988	Treated	WET	0.3	19	81	
	Treated	Totals	34	2700	10000	
	Untreated	WET	0.95	34.8	463	
2 /15 /1090		Totals	29.9	1750	3710	
2/15/1989	Treated	WET	ND	10.0 / 1.81	13.6	
		Totals	37.9	3340	7630	
	Untreated	WET	1.84	441	629	
2/16/1989		Totals	26.5	5200	6870	
_, _, _, _,	Treated	WET	ND	ND	0.16	
	rreated	Totals	21.2	4260	8330	
	Untreated	WET	1.71	28.1	640	
2/17/1989	onercacca	Totals	31.5	1550	7270	
2, 17, 1303	Treated	WET	ND	10.4	21.1	
	TTCUCCU	Totals	35.1	2040	8880	
	Untreated	WET	1.77	33.3	766	
2/21/1989	onercacea	Totals	24.9	1470	7070	
2/21/1909	Treated	WET	ND	12.6 / 3.15	61.7	
	i i eateu	Totals	34.5	2670	10500	
	Untreated	WET	1.76	1110	679	
2/22/1000	onci eated	Totals	26.1	22100	11300	
2/22/1989	Troated	WET	ND	ND	0.17	
	Treated	Totals	33.2	7830	8780	

SAMPLE			WET results in mg/L Total results in mg/kg				
DATE TYPE		ANALYSIS	Cd	Pb	Zn		
	Untreated	WET	2.25	44.30	717.00		
2 /22 /1000	Uncreated	Totals	42.5	2270	5170		
2/23/1989	Treated	WET	ND	20.9 / ND	22.0		
	Treated	Totals	24.6	3770	7680		
	Untreated	WET	1.68	71.1	635		
2/24/1989		Totals	28.3	1980	8650		
2/24/1909	Treated	WET	ND	0.73	0.16		
		Totals	28.9	7080	9980		
	Untreated	WET	1.49	120	511		
Mean	Untreated	Totals	37.5	2992	7962		
Values	Treated	WET	0.19	12.5	49.1		
	rreateu	Totals	31.6	2620	7084		
Treatment Reduction (as % of Untreated Conc.)		WET	87.0%	89.6%	90.4%		

N.D. = non-detect, or concentration less than lab reporting limit.

As noted by the bold figures at the bottom of Table 3 above, treatment efficiency for extractable cadmium, lead and zinc averaged between 87% and 90%.

Similar reductions were achieved for the four other metals that were evaluated (Cr, Cu, Hg and Ni). The average treatment reduction of extractable (WET) nickel was similar to the ratios expressed above for cadmium, lead and zinc. Extractable chromium and mercury values for untreated samples were too low to generate comparable reduction data in the treated samples. The fourth metal, copper, showed a slight increase in extractability with treatment, although all samples, both treated and untreated, were well below the STLC (25 mg/l).

B. RECENT ASR TREATABILITY STUDIES

More recent treatability studies have been conducted to evaluate the effectiveness of ASR treatment. Results of one such study are presented in the Table 4 and involve ASR conveyor belt samples collected before and after treatment.

Table 4

Recent Treatability Study Using Belt-Collected ASR Samples

		Tymo of	Parameter					
Sample Date	Sample Type	Type of Analysis	Cd (mg/L)	Pb (mg/L)	Zn (mg/L)			
4/23/2009	Untreated	WET	0.776	73.8	1170			
4/23/2009	Treated	WET	0.239	2.47	186			
4/23/2009	Untreated	WET	0.228	42.6	1050			
4/23/2009	Treated	WET	0.14	3.20	78.2			
4/23/2009	Untreated	WET	0.931	28.1	1420			
4/23/2009	Treated	WET	0.102	7.33	73.4			
Mean	Untreated	WET	0.645	48.17	1213			
Values Treate	Treated	WET	0.160	4.33	113			
	nt Reduction treated Conc.)	WET	75%	91%	91%			

Note: Samples were collected from ASR conveyor belt, before and after treatment, with pairs sampled approximately 5 minutes apart to allow for average pug mill treatment dwell time.

In addition to treatment studies involving one formulation of treatment chemicals, there is ongoing activity within the auto shredding industry to advance the efficacy of ASR treatment through formula modifications. This typically involves a collaborative effort between the manufacturer of the chemicals and the auto shredder.

Collaborative treatability studies between the chemical manufacturer and the auto shredder often involve applying various treatment protocols to bench scale samples. For example, 150 gram quantities of ASR taken from a 10,000 gram composite stockpile are common. The testing involves the application of various types and quantities of silicate blends and alkaline activators. Although each manufacturer claims to have a proprietary blend, the basic components are either potassium silicate or sodium silicate, combined with other additives such as phosphates and wetting agents. The original Lopat K20 blend that was developed in the 1980s contained three different viscosity potassium silicates, with borax and glycerin as additives. Thus, the goal has been to develop blends that provide the maximum effectiveness while minimizing the use of Portland cement or other alkaline activators.

During the past several years, one chemical manufacturer and a California auto shredder facility have collaborated to conduct a variety of ASR treatability studies concentrating on the target metals of cadmium, lead, copper, and zinc. The testing generally involved: (1) treating ASR with reformulated silicate blends (usually with sixteen aliquots and three or four alkaline activators), (2) measuring the metal concentrations in an accredited laboratory, and (3) selecting the most

promising combination for further evaluation. More than thirty different blends were evaluated using these basic parameters. A summary of these treatability results for varying polysilicate blends is provided in Table 5 below.

Table 5
Comparison of Treatment Formulations
(WET results, mg/L)

Formula	Date	Sample #	Cd	Pb	Zn	Cu	Application Sequence
	8/3/2009	1	ND	5.23	19.6	19.2	1nmet,10L
NMET	8/3/2009	3	0.094	7.63	21.2	6.14	1nmet,7C
INIVIEI	8/3/2009	5	0.079	16.3	25.6	17.9	2nmet,10L
	8/3/2009	6	0.332	7.21	118	20.1	2nmet,71
NIMETO CAN	11/12/2009	9	0.252	31.2	221	21.7	1nmet2,50w,10L
NMET2&W	11/12/2009	10	0.12	25.8	75.2	30.5	1nmet2,50w,7L
NMET3&W	11/12/2009	14	0.119	14.7	87.5	36.4	1nmet3,50W,7L
INIVIE I 3 & W	11/12/2009	16	0.12	15.3	93.8	36.2	1nmet3,50W,5L
NMET3GS	2/18/2010	5	ND	19.9	90.7	36.6	nmetgs,10L
NMET4	2/18/2010	9	ND	22.4	113	25.1	nmet4,10L
NIMETC	8/3/2009	9	ND	17.1	91.1	24.6	1nmeg,10L
NMETG	8/3/2009	13	0.051	12.9	55.8	20.1	2nmetg,10L
NMETNK	8/14/2000	1	ND	26.7	47.8	27.7	1nmetnk,10L
NMETIK	8/14/2009	5	0.407	2.74	208	4.96	2nmetnk,10L
NMETNKG	8/14/2009	9	ND	9.71	47.3	27.4	1nmet-,10L
NMETNKG	8/14/2009	13	ND	21.6	44.5	22.6	2nmet-10L
MET535G	8/21/2009	5	ND	67.6	187	22.3	met535g,10L
MEISSSG	8/21/2009	9	0.147	21.1	142	0.53	2met535g,10L
MET540	8/21/2009	13	0.116	7.24	65.1	0.622	1met540,10L
	7/28/2009	13	0.212	14.7	124	15.8	1kmet,10L
	7/28/2009	9	0.188	14.2	139	26.8	2kmet,10L
KMET	7/14/2009	1	0.075	4.19	25.8	2.51	2kmet,10L
	7/14/2009	3	0.333	1.59	105	1.88	2kmet,10C
	7/14/2009	8	ND	3.61	24.3	0.18	2kmet,10L
KMET&TRIA	10/26/2009	8	0.398	19.4	125	21.1	kmet,tria,7L
	7/14/2009	4	0.083	6.15	39.1	13	2k90,10L
	7/14/2009	7	ND	7.54	40.9	0.273	1,k90,10L
K90	7/14/2009	6	0.795	1.57	283	1.36	2k90,10C
	7/28/2009	5	0.147	16.3	153	29.4	1k90,10L
	7/28/2009	1	0.276	11.2	109	2.6	2k90,10L
IZOO 0 NI	7/14/2009	9	0.092	17.6	67	12.4	1k90,2n,10L
K90&N	7/14/2009	10	0.27	1.18	268	0.785	1k90,2n,10C
	7/9/2009	5nd	ND	10.6	89.7	1.06	1,2n1,10L
	7/9/2009	6	0.06	18.1	82.2	22.1	0,2n1,10L
N1	6/18/2009	7	ND	1.47	141	0.08	1,2n1,10L
	6/18/2009	4	ND	0.447	286	ND	2,1n1,10L
	7/21/2009	4	0.071	6.58	28.4	2.72	1n1,10L

Table 5
Comparison of Treatment Formulations
(WET results, mg/L)

	ı	ı	ı				
Formula	Date	Sample #	Cd	Pb	Zn	Cu	Application Sequence
N1&TRI	10/26/2009	1	0.234	4.09	73.7	2.57	1n1,1tr1,7L
N1A	5/19/2010	4	ND	49.5	51.5	20.4	n1a,10L
N1B	5/19/2010	8	0.112	26.9	34.9	22.3	n1b,10L
N1C	5/19/2010	12	ND	10.8	48.2	5.67	n1c,10L
N1D	5/19/2010	16	0.247	17.1	57.9	26.5	n1d,10L
MCX90N	8/21/2009	1	0.181	15.5	143	0.988	1mcx90n,10L
MCV00CC	2/9/2010	1	0.412	2.16	206	4.46	mcx90,10L
MCX90CS	2/9/2010	5	0.266	4.26	75.1	5.96	2mcx90,10L
MCX90CH	10/26/2010	4	0.317	16.4	109	56.8	mcx90,10L
MCX90N2B	2/18/2010	1	0.143	5.59	50.3	3.88	mcx90n2b,10L
MCX90N1&	1/25/2011	8	0.314	3.47	119	2.39	mcx90n1,10L
MCX90N1&M	4/28/2011	8	ND	0.119	168	0.169	mcx90n1,10M,5L
MCA90NT&M	4/28/2011	9	ND	0.844	157	0.806	mcx90n1,10M,5C
	8/23/2011	2	0.256	7.44	109	4.64	mcx90n1,1mtt,7L
MCX90N1&MTT	8/23/2011	4	0.159	2.91	112	3.12	mcx90n1,1mtt,10L
	9/14/2011	4	0.288	4.18	99.4	2.75	mcx90n1,1mtt,10L
MCV00N1 %MET	8/23/2011	6	ND	0.539	130	0.475	mcx90n1,1mft,7L
MCX90N1&MFT	9/14/2011	8	ND	5.54	53.6	1.54	mcx90n1,1mft,10L
	8/23/2011	10	ND	3.83	40.7	1.89	mcx90n1,10ltt,7L
MCX90N1<T	8/23/2011	12	ND	2.15	12.8	1.44	mcx90n1,10ltt,10L
	9/14/2011	12	ND	5.22	43.2	4.2	mcx90n1,10ltt,10L
PREA	10/20/2009	8	0.195	8.37	158	2.69	1.5prea,10L
RG	7/21/2009	5	0.166	12.9	134	22.9	2rg,10L
RGK	7/21/2009	6	0.7	4.5	41.9	2.17	2rgk,10L
RGS	7/21/2009	7	0.74	9.05	58.6	3.74	2rgs,10L
	7/21/2009	1	0.071	8.12	43.6	2.65	1ka,1kb,10L
Ka,Kb	7/21/2009	2	0.374	2.91	122	1.71	1ka,1kb,10C
	7/21/2009	3	1.1	1.98	246	1.5	1ka,1kb,10C/L
RUOH	9/9/2009	5	0.221	13.2	156	8.32	1ruoh,10L
КООП	10/20/2009	12	0.236	15.2	248	4.11	1ruoh,10L
K20A,K20B	11/12/2009	1	ND	24.6	132	36.9	1a,b,10L
	11/12/2009	5	0.147	112	173	42.9	1a,b,25w,10L
K20A,K20B&W	11/12/2009	6	0.215	39.7	92.6	35.9	1a,b,25w,7L
K20A&TSUL	11/4/2099	6	0.9	9.19	220	10.4	10k,28t,10L
125 A 9-D	7/21/2010	10	0.329	3.4	156	40.3	2,125ab,7L
125A&B	7/21/2010	12	ND	2.68	31.2	34.1	2,125ab,10L
STLC Values			1	50*	250	25	
(from CCR, Title 22	Ch. 11, § 6620	61.24)	1	50*	250	25	
Kon to table: ND-no	detection hele		::4 D.	11 + 024 4		40 40 04.14	s in excess of the STIC Fe

Key to table: ND=no detection, below reporting limit. Bold text represents results in excess of the STLC. For ASR, the de facto STLC for lead is 50 mg/l, as per the DTSC reclassification letters. The requirements of the reclassification letters vary with respect to other Title 22 metals.

VII. TREATED ASR - CHARACTERIZATION DATA REQUIRED BY LANDFILLS

The following section discusses landfill characterization data for treated ASR using either the standard or a modified WET method. Under the modified WET method, landfill leachate from the specific landfill that is receiving treated ASR is used as the extraction solution in lieu of the citrate buffer. For some landfills, the Waste Discharge Requirements may specify use of deionized water as the extraction solution.

A. LANDFILL LEACHATE TEST DATA

A summary of treated ASR results using landfill leachate (from Potrero Hills) as the extraction medium is provided in the following table.

Table 6
Summary of Landfill Leachate Testing of Treated ASR

SAMPLE DATE	Parameter											
	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Pb (mg/L)	Hg (mg/L)	Ni (mg/L)	Zn (mg/L)	Cr VI (mg/L)				
1/20/2009	< 0.05	< 0.050	0.45	< 0.100	< 0.005	0.20	0.18	< 0.020				
4/3/2009	< 0.050	< 0.050	0.06	< 0.100	< 0.005	0.236	0.275	< 0.020				
7/7/2009	< 0.050	< 0.050	< 0.05	< 0.100	< 0.005	0.123	0.201	< 0.020				
10/15/2009	< 0.050	< 0.100	0.165	< 0.100	< 0.100	0.142	0.351	< 0.100				
1/18/2010	< 0.020	< 0.100	1.2	< 0.100	< 0.100	0.217	< 0.100	< 0.100				
4/8/2010	< 0.020	< 0.100	1.25	< 0.100	< 0.005	0.147	< 0.100	< 0.020				

Note: purple cells represent results below laboratory reporting limit (N.D.).

In contrast to the results from standard WET method analysis, solubility testing conducted with landfill leachate (which is representative of actual conditions in the landfill, as opposed to the WET) shows little to no leachable heavy metals in the treated ASR.

C. TREATED ASR CHARACTERIZATION DATA (TOTAL AND WET)

Table 7 presents Total and extractable data gathered between January 2009 and January 2012 as part of routine characterization testing of treated ASR conducted by California auto shredders. Many of these analyses were required by the reclassification letters issued to certain of the shredder facilities and/or by the Waste Discharge Requirements or other permits for certain landfills that accept treated ASR for use as alternative daily cover. In some cases, WET data is required to be submitted to the landfills on a quarterly basis, as part of existing alternative daily cover acceptance agreements between the landfills and the individual auto shredders.

Table 7 - Total and WET Results for Treated ASR

	Total							WET							
SAMPLE DATE	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Pb (mg/L)	Hg (mg/L)	Ni (mg/L)	Zn (mg/L)	
1/7/2009	-	-	-	690	-	-	-	-	-	-	35	-	-	-	
1/16/2009	< 0.5	408	4390	835	0.890	< 2.5	9950	< 0.1	1.03	6.12	6.27	< 0.02	0.625	144	
1/16/2009	16	110	37000	1000	0.89	150	11000	0.11	0.84	9.8	1.4	0.0017	0.96	22	
1/16/2009	< 0.5	56.2	5350	1110	1.02	< 2.5	15000	< 0.1	0.669	9.91	4.70	< 0.02	0.565	34.7	
4/10/2009	19.4	77.9	807	1040	2.48	184	11100	0.073	0.688	6.04	2.17	< 0.02	0.589	31.3	
4/11/2009	12.7	103	1010	991	1.64	145	9140	0.109	0.816	7.92	6.96	< 0.02	0.680	94.1	
5/26/2009	< 0.5	84.7	16300	3340	0.991	258	11500	< 0.1	0.948	10.6	10.4	< 0.01	0.638	48.9	
7/2/2009	-	ı	-	150	-	1	-	-	-	1	22.0	-	-	-	
7/2/2009	-	-	-	910	-	•	-	-	-	-	51.0	-	•	-	
7/10/2009	65.4	83.9	16300	1360	0.300	< 2.5	10500	< 0.1	1.13	7.76	7.08	< 0.01	0.593	52.0	
7/17/2009	183	217	10800	1420	1.23	305	15100	0.313	1.15	16.6	3.49	< 0.01	0.860	94.5	
7/18/2009	58.2	100	333	1010	0.823	< 2.5	8980	< 0.1	0.889	4.30	4.63	< 0.02	0.758	154	
10/2/2009	< 0.5	137	2150	1400	0.499	390	11700	< 0.1	1.10	12.1	6.17	< 0.02	< 0.3	38.8	
10/9/2009	< 0.5	150	3520	1060	1.07	286	8720	0.085	1.00	5.87	6.11	< 0.01	< 0.3	32.0	
10/10/2009	< 0.5	81.5	707	1020	0.647	< 2.5	11170	0.038	0.841	7.26	3.99	< 0.02	< 0.3	32.6	
2/1/2010	-	-	-	1284	-	-	-	-	-	-	39.16	-	-	-	
2/1/2010	-	-	-	901	-	-	-	-	-	-	4.86	-	-	-	
2/1/2010	-	-	-	2577	-	-	-	-	-	-	47.24	-	-	-	
2/3/2010	< 0.5	136	2100	1810	2.60	< 2.5	9540	0.358	1.84	8.42	2.64	< 0.01	1.17	123	
2/5/2010	< 0.5	113	1920	785	8.15	< 2.5	9140	< 0.1	1.62	8.04	14.3	< 0.02	< 0.3	58.2	
2/6/2010	< 0.5	121	17600	843	2.42	< 2.5	6470	0.152	1.30	12.4	1.37	< 0.01	0.846	38.2	
4/9/2010	< 0.5	118	976	1160	1.65	< 2.5	10900	0.372	1.08	5.59	5.13	< 0.02	0.947	198	
4/10/2010	< 0.5	196	3440	1440	2.45	311	14300	0.075	0.769	10.9	6.93	< 0.02	1.09	46.5	
4/12/2010	< 0.5	114	17100	1330	0.581	< 2.5	10600	0.121	0.725	8.76	1.43	< 0.01	0.646	22.1	
7/7/2010	< 0.5	173	7300	6450	1.15	269	16400	0.065	0.976	23.7	6.64	< 0.01	0.563	28.7	
7/10/2010	< 0.5	154	20400	830	1.67	< 2.5	9180	< 0.050	0.843	6.71	1.13	< 0.01	0.751	11.0	
7/16/2010	10.1	160	8610	681	1.27	337	8000	0.659	1.54	1.43	3.97	< 0.01	1.97	233	
7/26/2010	-	-	-	2600	-	-	-	-	-	-	3.20	-	-	-	
7/26/2010	-	-	-	740	-	-	-	-	-	-	4.30	-	-	-	
7/26/2010	-	-	-	700	-	-	-	-	-	-	5.60	-	-	-	

Table 7 - Total and WET Results for Treated ASR

	Total							WET							
SAMPLE DATE	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Pb (mg/L)	Hg (mg/L)	Ni (mg/L)	Zn (mg/L)	
10/9/2010	18.9	82.3	2740	879	0.558	141	8570	0.233	1.33	7.21	2.64	< 0.01	0.839	45.6	
10/9/2010	10.6	62.9	870	469	1.49	122	5430	< 0.1	0.697	8.49	1.17	< 0.01	0.742	5.62	
10/21/2010	20.6	68.5	3260	997	1.24	182	11900	< 0.1	0.756	11.6	2.10	< 0.01	0.605	12.7	
1/7/2011	7.12	84.8	240	400	0.702	92.8	6300	< 0.1	0.902	4.18	1.41	< 0.01	0.496	11.3	
1/7/2011	21.7	88.0	2040	854	0.312	159	9530	0.056	1.13	14.4	2.11	< 0.02	0.575	8.59	
1/8/2011	15.2	86.9	2190	742	0.617	159	7730	< 0.1	0.900	4.40	0.637	< 0.01	0.534	4.30	
1/12/2011	1	1	-	630	-	•	-	•	-	ı	11.0	-	•	-	
1/12/2011	ı	ı	-	360	-	•	-	ı	-	ı	4.10	-	ı	-	
1/12/2011	1	-	-	360	-	1	-		-	1	28.0	-	-	-	
4/9/2011	15.5	132	7030	731	1.11	108	7750	< 0.1	0.719	4.09	2.27	< 0.02	0.467	16.1	
4/9/2011	16.0	104	1290	1150	1.55	188	8380	0.190	1.31	4.63	2.07	< 0.01	0.758	111	
4/15/2011	50.3	91.4	412	957	0.578	138	7650	0.097	0.758	13.0	6.46	< 0.02	0.775	118	
7/6/2011	-	-	-	1000	-	•	-	-	-	-	< 0.25	-	•	-	
7/6/2011	•	•	-	1000	-	•	-	•	-	1	0.48	-	•	-	
7/6/2011	•	1	-	1100	-	•	-	•	-	ı	2.00	-	•	-	
7/9/2011	7.72	496	5670	433	0.966	135	3630	< 0.1	0.606	7.57	1.58	< 0.01	0.554	7.29	
7/15/2011	18.4	76.4	17000	1400	0.768	145	8190	< 0.1	1.00	6.47	1.30	< 0.02	0.435	3.97	
7/23/2011	15.5	67.9	6810	711	1.25	153	9370	< 0.1	0.622	6.63	4.32	< 0.01	0.567	22.6	
10/5/2011	7.88	41.7	750	449	0.252	51.3	3310	0.086	0.934	12.8	0.753	< 0.02	0.390	7.22	
10/7/2011	8.33	43.3	368	665	0.474	140	6090	0.038	0.631	6.25	6.01	< 0.01	5.24	31.4	
10/8/2011	12.7	66.2	14800	877	0.794	429	9090	< 0.1	0.821	5.18	1.07	< 0.01	0.514	6.15	
1/20/2012	-	-	-	970	-	-	-	-	-	-	0.81	-	-	-	
1/20/2012	-	-	-	1100	-	-	-	-	-	-	6.20	-	-	-	
1/20/2012	-	-	-	920	-	•	-	-	-	-	0.54	-	-	-	
# in Data Set	36	36	36	54	36	36	36	36	36	36	54	36	36	36	
90% UCL Value	27.0	142.2	8966	1499	1.56	185	10114	0.137	1.035	9.55	12.2	< 0.02	1.22	69.2	
TTLC / STLC	100	2500	2500	1000	20	2000	5000	1	*5 / 560	25	50	0.2	20	250	

Notes: USEPA ProUCL Software Version 4.1.01 was used to calculate 90% UCL values. Non-detect values were included in UCL data sets, and distribution model recommended by program for 95% UCL was used for each set. The results shown in the purple cells are below the lab reporting limit. **Bold** values are in excess of standards.

^{*} The STLC standard for Cr VI is 5 mg/l, whereas the Total or Cr III STLC for samples passing the TCLP test is 560 mg/l. NA=not applicable, highest ND value used instead.

Treatment of ASR May 2012

The preceding Table 7 of total and WET Results for Treated ASR includes a minimum of 36 sample sets, for seven Total and WET-extractable metals, collected over a 3-year period. Eighteen additional Total and WET-extractable lead-only results from a California shredder during the same period were also included in the data set.

USEPA's ProUCL Software Version 4.1.01 was utilized to calculate the 90% Upper Confidence Limits (90% UCLs) for each metal in the sample data set (USEPA, 2011b). This statistical value is intended to represent the upper limit (with 90% confidence) of the true mean of any randomly drawn subsets of the data. Comparison of total concentrations of metals in the untreated ASR with extractable concentrations in the treated material clearly demonstrates the effectiveness of the ASR treatment process.

VIII. CONCLUSIONS

This report has been prepared at the request of the California Chapter of the Institute of Scrap Recycling Industries (ISRI) to objectively evaluate whether the auto shredder residue (ASR) treatment process currently employed at three California shredders effectively reduces the amount of extractable metals in ASR, such that treated ASR is suitable for disposal or beneficial use as Alternative Daily Cover in nonhazardous waste landfills. The ASR treatment process involves the use of soluble silicates in an aqueous solution, in combination with dry cement or another alkaline activator, which alters the chemical characteristics of leachable heavy metals in the ASR matrix. This treatment technology is known to the USEPA as *Stabilization*, and has been studied and shown to be effective on a wide range of constituents including heavy metals (USEPA, 2009).

Treatability studies by Dr. Trezek and others on the specific use of this technology for treatment of ASR began in the early 1980s, and concluded that the extractability of lead, cadmium, zinc and other heavy metals can be reduced by 90% to 99% with the use of this technology. These treatability study findings were submitted to DTSC and, on that basis, DTSC determined that treated ASR was eligible for reclassification on the grounds that it possesses mitigating physical and chemical characteristics that render it insignificant as a hazard to human health and the environment. The current review demonstrates that the earlier reclassification decision continues to be supported by analytical data related to the extractability of heavy metals (primarily lead, cadmium and zinc) in the waste before and after treatment.

IX. REFERENCES

- C.C.I., a Chemical Corporation, of Vernon, California, (2011). Corporate information downloaded from home page available at: http://www.ccichemical.com/
- CEMEX, Material Safety Data Sheet (MSDS) for Portland cement, (2011). Downloaded from http://wstabilization.com/download/files/Cemex%20%20MSDS.pdf
- Cullinane, M.J.; Jones, L.W.; Malone, P.G.; (1986). *Handbook for the Stabilization/Solidification of Hazardous Waste*, USEPA, document EPA/540/2-86/001, Table 2-2.
- Davis, E.L.; Krumrine, P.H.; Boyce, J.S.; Falcone, J.S.; (1986). *Mechanisms for the Fixation of Heavy Metals in Solidified Wastes Using Soluble Silicates*; PQ® Corporation, presented at the HWHM '86 Conference in Atlanta, Georgia.
- DeGaspari, John. (1999). "From trash to cash: A new process reclaims former unrecoverables in the residue of scrapped vehicles." *Mechanical Engineering Magazine Online* http://www.memagazine.org/backissues/membersonly/june99/features/trash/trash.html.
- Envirokem, (2008). Product Bulletin for Metbond MCX-90, document #TBR-90-1, undated but issued to shredder facility on 12-1-2008.
- Hook, Brian R. (2008). "Auto shredder residue recycling researched." AmericanRecycler.com, http://www.americanrecycler.com/1008/auto.shtml.
- Institute of Scrap Recycling Industries (ISRI), (2011). "The Scrap Recycling Industry: Ferrous Scrap" factsheet.
- Interstate Technology and Regulatory Cooperation (ITRC) Working Group, (1997). "Emerging Technologies for the Remediation of Metals in Soils; in situ Stabilization/in place Inactivation".
- Krofchak, D, (1979). "Solidification of Wastes", Chapter 17, Toxic and Hazardous Waste Disposal, Vol. 1, Ann Arbor Science.
- Metal Bulletin Daily, (2008). "(AMM) VRP Research Narrowing the auto recycling gap," Issue 96, 1/1/2008.
- PQ® Corporation, (2011). *Waste Treatment* webpage, available at http://www.pqcorp.com/pc/NorthAmerica/Markets/WasteTreatment.aspx.

- Trezek, G.J., (1994). *Remediation of Heavy Metal Contaminated Solids Using Polysilicates*, Chapter 20, of Process Engineering for Pollution Control and Waste Minimization, edited by Wise, D.L. and Trantolo, D.J., Marcel Dekker, Inc., New York, NY.
- USEPA, (1980). *Guide to the Disposal of Chemically Stabilized and Solidified Waste* (SW-872, NTIS: PB87-154 902).
- USEPA, (1986). SW846 Method 1320, Multiple Extraction Procedure, Revision 0.
- USEPA, (2003). Guide for Industrial Waste Management, EPA/530/R-03/001.
- USEPA, (2006). *In Situ Treatment Technologies for Contaminated Soil*, Engineering Forum Issue Paper, document EPA/542/F-06/013.
- USEPA, (2008). *Overview of Portland Cement and Concrete*, Appendix A of Study on Increasing the Usage of Recovered Mineral Components in Federally Funded Projects Involving Procurement of Cement or Concrete ... Report to Congress. Document EPA530-R-08-007, download at http://www.epa.gov/wastes/conserve/tools/cpg/pdf/rtc/report4-08.pdf
- USEPA, (2009) Technology Performance Review: Selecting and Using Solidification/ Stabilization Treatment for Site Remediation, document EPA/600/R-09/148.
- USEPA, (2011a). Materials Characterization Paper In Support of the Final Rulemaking: Identification of Nonhazardous Secondary Materials That Are Solid Waste Auto Shredder Residue, EPA-HQ-RCRA-2008-0329-18.
- USEPA, (2011b). ProUCL Version 4.1.01 Software, Technical Support Center for Monitoring and Site Characterization webpage, download at http://www.epa.gov/osp/hstl/tsc/software.htm.