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Standard Guide for Use of Coal Combustion Products for Solidification/ Stabilization of Inorganic Wastes¹

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1. Scope

1.1 This guide covers methods for selection and application of coal combustion products (CCPs) for use in the chemical stabilization of trace elements in wastes and wastewater. These elements include, but are not limited to, arsenic, barium, boron, cadmium, chromium, cobalt, lead, molybdenum, nickel, selenium, vanadium, and zinc. Chemical stabilization may be accompanied by solidification of the waste treated. Solidification is not a requirement for the stabilization of many trace elements, but does offer advantages in waste handling and in reduced permeability of the stabilized waste.

1.1.1 Solidification is an important factor in treatment of wastes and especially wastewaters. Solidification/Stabilization (S/S) technology is often used to treat wastes containing free liquids. This guide addresses the use of CCPs as a stabilizing agent without the addition of other materials; however, stabilization or chemical fixation may also be achieved by using combinations of CCPs and other products such as lime, lime kiln dust, cement kiln dust, cement, and others. CCPs used alone or in combination with other reagents promote stabilization of many inorganic constituents through a variety of mechanisms. These mechanisms include precipitation as carbonates, silicates, sulfates, and so forth; microencapsulation of the waste particles through pozzolanic reactions; formation of metal precipitates; and formation of hydrated phases (1-4).² Long-term performance of the stabilized waste is an issue that must be addressed in considering any S/S technology. In this guide, several tests are recommended to aid in evaluating the long-term performance of the stabilized wastes.

1.2 The CCPs that are suited to this application include fly ash, spent dry scrubber sorbents, and certain advanced sulfur control by-products from processes such as duct injection and fluidized-bed combustion (FBC).

1.3 The wastes or wastewater, or both, containing the problematic inorganic species will likely be highly variable, so the chemical characteristics of the waste or wastewater to be treated must be determined and considered in the selection and application of any stabilizing agent, including CCPs. In any waste stabilization process, laboratory-scale tests for compatibility between the candidate waste or wastewater for stabilization with one or more selected CCPs and final waste stability are recommended prior to full-scale application of the stabilizing agent.

1.4 This guide does not intend to recommend full-scale processes or procedures for waste stabilization. Full-scale processes should be designed and carried out by qualified scientists, engineers, and environmental professionals. It is recommended that stabilized materials generated at the full-scale stabilization site be subjected to testing to verify laboratory test results.

1.5 The utilization of CCPs under this guide is a component of a pollution prevention program; Guide E1609 describes pollution prevention activities in more detail. Utilization of CCPs in this manner conserves land, natural resources, and energy.

1.6 This guide applies only to CCPs produced primarily from the combustion of coal. It does not apply to ash or other combustion products derived from the burning of waste; municipal, industrial, or commercial garbage; sewage sludge or other refuse, or both; derived fuels; wood waste products; rice hulls; agricultural waste; or other noncoal fuels.

1.7 Regulations governing the use of CCPs vary by state. The user of this guide has the responsibility to determine and comply with applicable regulations.

1.8 It is recommended that work performed under this guide be designed and carried out by qualified scientists, engineers, and environmental professionals.

¹ This guide is under the jurisdiction of ASTM Committee E50 on Environmental Assessment, Risk Management and Corrective Action and is the direct responsibility of Subcommittee E50.03 on Pollution Prevention/Beneficial Use.

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² The boldface numbers in parentheses refer to the list of references at the end of the text.

1.9 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards:³

- C114 Test Methods for Chemical Analysis of Hydraulic Cement
- C311 Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete
- C400 Test Methods for Quicklime and Hydrated Lime for Neutralization of Waste Acid
- D75 Practice for Sampling Aggregates
- D422 Test Method for Particle-Size Analysis of Soils
- D558 Test Methods for Moisture-Density (Unit Weight) Relations of Soil-Cement Mixtures
- D653 Terminology Relating to Soil, Rock, and Contained Fluids
- D1556 Test Method for Density and Unit Weight of Soil in Place by Sand-Cone Method
- D1633 Test Methods for Compressive Strength of Molded Soil-Cement Cylinders
- D1635 Test Method for Flexural Strength of Soil-Cement Using Simple Beam with Third-Point Loading
- D2166 Test Method for Unconfined Compressive Strength of Cohesive Soil
- D2216 Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass
- D2922 Test Methods for Density of Soil and Soil-Aggregate in Place by Nuclear Methods (Shallow Depth) (Withdrawn 2007)⁴
- D2937 Test Method for Density of Soil in Place by the Drive-Cylinder Method
- D3441 Test Method for Mechanical Cone Penetration Tests of Soil (Withdrawn 2014)⁴
- D3877 Test Methods for One-Dimensional Expansion, Shrinkage, and Uplift Pressure of Soil-Lime Mixtures
- D3987 Practice for Shake Extraction of Solid Waste with Water
- D4318 Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils
- D4842 Test Method for Determining the Resistance of Solid Wastes to Freezing and Thawing (Withdrawn 2006)⁴
- D4843 Test Method for Wetting and Drying Test of Solid Wastes
- D4972 Test Method for pH of Soils
- D5084 Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter
- D5239 Practice for Characterizing Fly Ash for Use in Soil Stabilization
- E1609 Guide for Development and Implementation of a Pollution Prevention Program (Withdrawn 2010)⁴

3. Terminology

3.1 Definitions:

3.1.1 Definitions are in accordance with Terminology **D653**.³

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *advanced sulfur control (ASC) products*— by-products generated from advanced coal conversion technologies including FBC and gasification and by-products from advanced environmental emissions cleanup technologies such as duct injection and lime injection multiphase burners (LIMB).

3.2.2 *baghouse*—a facility constructed at some coal-fired power plants consisting of fabric filter bags that mechanically trap particulates (fly ash) carried in the flue gases.

3.2.3 *beneficial use*—projects promoting public health and environmental protection, offering equivalent success relative to other alternatives, and preserving natural resources.

3.2.4 *BDAT*—best demonstrated available technology.

3.2.5 *boiler slag*—a molten ash collected at the base of slag tap and cyclone boilers that is quenched in a water-filled hopper and shatters into black, angular particles having a smooth, glassy appearance.

3.2.6 *bottom ash*—agglomerated ash particles formed in pulverized coal boilers that are too large to be carried in the flue gases and impinge on the boiler walls or fall through open grates to an ash hopper at the bottom of the boiler. Bottom ash is typically grey-to-black in color, is quite angular, and has a porous surface texture.

3.2.7 *coal combustion products*—fly ash, bottom ash, boiler ash, or flue gas desulfurization (FGD) material resulting from the combustion of coal.

3.2.8 *DSC*—differential scanning calorimetry.

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ The last approved version of this historical standard is referenced on www.astm.org.

3.2.9 *DTA*—differential thermal analysis.

3.2.10 *DTG*—differential thermal gravimetry.

3.2.11 *electrostatic precipitator*—a facility constructed at some coal-fired power plants to remove particulate matter (fly ash) from the flue gas by producing an electric charge on the particles to be collected and then propelling the charged particles by electrostatic forces to collecting curtains.

3.2.12 *encapsulation*—complete coating or enclosure of a toxic particle by an additive so as to sequester that particle from any environmental receptors that may otherwise have been negatively impacted by that particle.

3.2.13 *ettringite*—a mineral with the nominal composition $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$. Ettringite is also the family name for a series of related compounds, known as a mineral group or family, which includes the following minerals (1):

Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$
Charlesite	$\text{Ca}_6(\text{Si,Al})_2(\text{SO}_4)_2(\text{B}[\text{OH}]_4)(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$
Sturmanite	$\text{Ca}_6\text{Fe}_2(\text{SO}_4)_2(\text{B}[\text{OH}]_4)(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$
Thaumasite	$\text{Ca}_6\text{Si}_2(\text{SO}_4)_2(\text{CO}_3)_2(\text{OH})_{12} \cdot 24\text{H}_2\text{O}$
Jouravskite	$\text{Ca}_6\text{Mn}_2(\text{SO}_4)_2(\text{CO}_3)_2(\text{OH})_{12} \cdot 24\text{H}_2\text{O}$
Bentorite	$\text{Ca}_6(\text{Cr,Al})_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$

3.2.14 *flue gas desulfurization material*—a by-product of the removal of the sulfur gases from the flue gases, typically using a high-calcium sorbent such as lime or limestone. Sodium-based sorbents are also used in some systems. The three primary types of FGD processes commonly used by utilities are wet scrubbers, dry scrubbers, and sorbent injection. The physical nature of these by-products varies from a wet, thixotropic sludge to a dry powdered material, depending on the process.

3.2.15 *fly ash*—coal ash that exits a combustion chamber in the flue gas. Coal fly ashes are typically pozzolans. Some coal fly ashes also exhibit self-hardening properties in the presence of moisture.

3.2.16 *pozzolans*—siliceous or siliceous and aluminous materials that in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxides at ordinary temperatures to form compounds possessing cementitious properties.

3.2.17 *S/S*—solidification/stabilization.

3.2.18 *stabilization or fixation*—immobilization of undesirable constituents to limit their introduction into the environment. Toxic components are immobilized by treating them chemically to form insoluble compounds.

3.2.19 *solidification*—the conversion of soils, liquids, or sludges into a solid, structurally sound material for disposal or use, typically referring to attainment of 50 psi or strength of surrounding soil.

3.2.20 *XRD*—x-ray diffraction.

4. Significance and Use

4.1 *General*—CCPs can have chemical and mineralogical compositions that are conducive to use in the chemical stabilization of trace elements in wastes and wastewater. These elements include, but are not limited to, arsenic, barium, boron, cadmium, chromium, cobalt, lead, molybdenum, nickel, selenium, vanadium, and zinc. Chemical stabilization may be accompanied by solidification of the waste treated. Solidification is not a requirement for the stabilization of many trace elements, but does offer advantages in waste handling and in reduced permeability of the stabilized waste. This guide addresses the use of CCPs as a stabilizing agent without addition of other materials. S/S is considered the BDAT for the disposal of some wastes that contain metals since they cannot be destroyed by other means (2).

4.1.1 *Advantages of Using CCPs*—Advantages of using CCPs for waste stabilization include their ready availability in high volumes, generally good product consistency from one source, and easy handling. CCPs vary depending on the combustion or emission control process and the coal or sorbents used, or both, and CCPs contain trace elements, although usually at very low concentrations. CCPs are generally an environmentally suitable materials option for waste stabilization, but the compatibility of a specific CCP must be evaluated with individual wastes or wastewater through laboratory-scale tests followed by full-scale demonstration and field verification. CCPs suitable for this chemical stabilization have the ability to incorporate large amounts of free water into hydration products. CCPs that exhibit high pHs (>11.5) offer advantages in stabilizing trace elements that exist as oxyanions in nature (such as arsenic, boron, chromium, molybdenum, selenium, and vanadium) and trace elements that form oxyhydroxides or low-solubility precipitates at high pH (such as lead, cadmium, barium, and zinc). Additionally, CCPs that exhibit cementitious properties offer advantages in solidifying CCP-waste mixtures as a result of the hydration reactions of the CCP. These same hydration reactions frequently result in the formation of mineral phases that stabilize or chemically fix the trace elements of concern.

4.2 *Chemical/Mineralogical Composition*—Since CCPs are produced under conditions of high temperature, reactions with water during contact with water or aqueous solutions can be expected. Mineral formation may contribute to the chemical fixation and/or solidification achieved in the waste stabilization process. One example of this type of chemical fixation is achieved by ettringite formation. Reduced leachability of several trace elements has been correlated with ettringite formation in hydrated high-calcium CCPs typically from U.S. lignite and subbituminous coal, FGD materials, and ASC by-products. These materials are the best general candidates for use in this chemical fixation process. Lower-calcium CCPs may also be effective with addition of

a calcium source that maintains the pH above 11.5. Ettringite forms as a result of hydration of many high-calcium CCPs, so adequate water must be available for the reaction to occur. The mineral and amorphous phases of CCPs contribute soluble elements required for ettringite formation, and the ettringite formation rate can vary based on the mineral and amorphous phase compositions.

4.3 *Environmental Considerations:*

4.3.1 *Regulatory Framework:*

4.3.1.1 *Federal*—In 1999, EPA completed a two-phased study of CCPs for the U.S. Congress as required by the Bevill Amendment to RCRA. At the conclusion of the first phase in 1993, EPA issued a formal regulatory determination that the characteristics and management of the four large-volume fossil fuel combustion wastestreams (that is, fly ash, bottom ash, boiler slag, and flue gas emission control waste) do not warrant hazardous waste regulation under RCRA and that utilization practices for CCPs appear to be safe. In addition, EPA “encourage[d] the utilization of coal combustion byproducts and support[ed] State efforts to promote utilization in an environmentally beneficial manner.” In the second phase of the study, EPA focused on the byproducts generated from FBC boiler units and the use of CCPs from FBC and conventional boiler units for mine reclamation, among other things. Following completion of the study, EPA issued a regulatory determination in April 2000 that again concluded that hazardous waste regulation of these combustion residues was not warranted. There is currently no regulatory program at the federal level that addresses the utilization of CCPs. The wastes or wastewater requiring stabilization may fall under federal jurisdiction, so the final stabilized material may need to be evaluated and disposed of according to federal regulations. Potentially applicable federal regulations may include the Resource Conservation and Recovery Act (RCRA), Hazardous Solid Waste Act (HSWA), Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and Superfund Amendment and Reauthorization Act (SARA). A brief description of these regulations is included in the EPA document, entitled *Stabilization/Solidification of CERCLA and RCRA Wastes: Physical Tests, Chemical Testing Procedures, Technology Screening, and Field Activities* (2) and have been summarized by ACAA (5). The EPA document states “stabilization/solidification is a proven technology for the treatment of hazardous wastes and hazardous waste sites.” According to EPA (2), stabilization/solidification is the BDAT for the disposal of some metals since they cannot be destroyed by other means. Provisions in federal laws list requirements that land disposal of hazardous wastes is only acceptable if these wastes are treated with the BDAT or with technology that meets or exceeds the treatment level of BDAT. Wastes that contain free liquids are prohibited from land disposal by federal RCRA regulations or by equivalent state regulations, or both. The chemical binding of free liquids brought about by solidification allows wastes that fail the EPA Paint Filter Test (EPA Method 9095-SW846) (6) to be land-disposed after successful S/S treatment.

4.3.1.2 A summary of coal fly ash utilization in waste stabilization/solidification, including a discussion of environmental/regulatory issues, demonstrations, and commercial applications, has been prepared (5).

4.3.1.3 *State*—Some states do not have specific regulations addressing the use of CCPs, and requests for CCP use are handled on a case-by-case basis or under generic state recycling laws or regulations. Some states have adopted laws and regulations or issued policies and/or guidance regarding CCP use, but CCP use varies widely within these states (7). Waste or wastewater requiring stabilization and the final stabilized material may also be regulated by individual states, so these regulations need to be identified and followed. Many states are authorized to manage the hazardous waste management programs within their state. RCRA and HSWA statutes allowed the states to become authorized by EPA. It is therefore extremely likely that S/S-treated waste will be regulated by a state.

5. CCP Characterization

5.1 *General*—Characterization of the CCP(s) under consideration for use as a stabilizing agent is needed to determine bulk chemical and mineralogical composition to form ettringite when hydrated and that sufficient alkalinity is available to maintain a high pH.

5.2 *Sampling and Handling*—Sampling CCPs for testing purposes should conform to Practice D75 or Test Method C311 as appropriate. Proper laboratory protocols for handling fine material should be followed.

5.3 *Chemical Composition*—Test Method C311 is often used to determine the major chemical constituents of CCP samples. The most critical constituents requiring quantitation are calcium, aluminum, and sulfur.

5.4 *pH*—Test Method D4972 or Practice D5239 may be used to determine CCP pH. In assessing the test results, consideration should be given to the possibility that the pH of the CCP may differ with age, water content, and other conditions. EPA Method SW-9045 (8) is also applicable.

5.5 *Buffer Capacity*—The buffer capacity of the CCP is important in maintaining the high pH that generally is a requirement for the stabilization mechanisms of interest when CCPs are used as stabilization agents. The CCP must have enough buffer capacity to maintain the pH of the stabilized waste in the appropriate range so the waste remains stable over time and under environmental stresses. Test Method C400 can be applied to evaluate the buffer capacity of the CCP. Determine the basicity factor for the CCP as noted in Test Method B of Test Method C400.