

**Announcing a new process for Removal of Reactive Metals from Metal Surfaces**

**Alkali Metals AND Ammonia (AMANDA)**

Many decommissioned nuclear reactor facilities are challenged with removal of legacy waste streams that contain reactive metals, especially metallic sodium. Many years of development of methods for treatment of reactive metals have occurred and are proceeding slowly. Methods have included controlled reactions of alkali metals with water, steam, and carbon dioxide.

In November 2009, Commodore Advances Sciences, Inc. conducted a successful demonstration at our facility in Oak Ridge, Tennessee, which was subsequently reported in detail. The report provides a detailed process for using the Alkali Metals and Ammonia (AMANDA) process to treat reactive metal-contaminated components from decommissioning of sodium-cooled nuclear reactors.

This report concludes that:

1. AMANDA is uniquely suited as an alkali metals treatment and conversion process.
2. AMANDA is superior to other alkali metals treatment technologies.
3. AMANDA is much faster and therefore less expensive than conventional treatment processes for removal of reactive metals from metal surfaces.
4. AMANDA is an inherently safer treatment technology, and removes alkali metals rather than passivating them in place (usually with steam).
5. AMANDA is based on a mature process with fourteen years of campaign experience and can be quickly mobilized for onsite operation.
6. AMANDA has enhanced capabilities to treat target materials beyond alkali metals.

Commodore has determined that beneficial recycling of items currently stored as waste streams at decommissioned sodium-cooled nuclear reactors worldwide is feasible instead of waste disposal at a regulated landfill. Therefore, materials shipped from reactors to Commodore are to be treated as product unless determined otherwise through operations. Metals are recyclable through a melting process, and alkali metal compounds in solution are recyclable through wet neutralization processes at Commodore facilities. Very little waste volume is generated relative to received material.

The patented Solvated Electron Technology (SET™) process is adapted for this demonstration task as a means to show how both residual and bulk alkali metals can be removed from sodium-cooled reactor components in a safe, fast and cost effective manner, with minimal risk to onsite workers and no risk to the public. SET™ is a non-thermal alternative to waste incineration that was designed to treat mixed waste and hazardous soils and liquids to enable land fill disposal. It has been deployed commercially at many DOE, DOD, and commercial sites throughout the USA since 1995. In these deployments, sodium is injected into the system as a reagent, which dissolves in ammonia prior to the addition of waste materials. The solvated

ammonia solutions attack the chemical components of the waste materials to destroy the hazardous constituents (Solvated Electron Technology (SET™), U.S. Patent No. 6,049,021).

Given that sodium is readily soluble in anhydrous ammonia, it is clear that sodium attached to metallic items would also be dissolved upon contact with ammonia. Therefore, by ignoring the back end of the SET™ process, where waste materials are added to the solvated solution, a solvated solution is instead created by adding ammonia to sodium-contaminated components. The solvated solution is then treated to a suitable waste or product form by established chemical techniques. The primary output is a manageable sodium compound, NaOH. This is the principle behind the Alkali Metals and Ammonia (AMANDA) process. The process is applicable to all alkali metals commonly used industrially, including sodium, lithium, potassium, NaK, calcium, and cesium.

### ***Process Chemistry***

The AMANDA process is based upon a chemical phenomenon discovered by Sir Humphrey Davy in 1865:



The valence electron of the sodium atom is released to the ammonia and exists in a relatively rare but stable state unassociated with an atom. It is believed that the ammonia molecules form “cages” surrounding each electron, trapping the electrons in the solution. In this state, both the electrons and the sodium atoms are available to react with other elements and compounds. The indicators of a solvated solution are its color and its conductivity. A solvated solution is dark blue, as shown in Figure 1, and it is highly conductive. Solvated electron solutions are regarded as solutions of the metallic cation and electrons, with a conductivity approaching that of liquid metals. In an almost titration-like fashion, both color and conductivity disappear when the electrons (and the free sodium atoms) are reacted. Both these indicators are easily measured, and are included in process instrumentation where appropriate.

The AMANDA process commercially treats sodium (or alkali metals) by applying basic chemistry in three steps:

**Step 1** – create solvated solution by adding ammonia to sodium contaminated waste items (or by injecting liquid bulk sodium into ammonia).



This provides the dark blue, highly conductive solvated solution, and in AMANDA is performed in a closed system.

**Step 2** – convert solvated solution to caustic and recover ammonia.



This causes secondary hydrogen generation, which is controlled by the rate and volume of water addition. The presence of ammonia vapor inerts the atmosphere as hydrogen is

generated. Pressure controls effect the recovery of ammonia through a refrigeration system to a holding tank, while hydrogen is released with some ammonia vapor through the off gas equipment.

The amount of ammonia vapor released during system venting operations is very small (nominally less than 10lbs/day), an order of magnitude below regulatory requirements (typically, 100lb/day). Neutralizing the ammonia creates a salt which must ultimately be disposed. Alternatively, allowing the gas to escape to the atmosphere in a controlled manner does not generate a disposal stream. This, of course, may cause a detectable ammonia odor in the vicinity of the discharge stack, which may or may not be acceptable at the treatment location. However, the discharge volume is controlled well within regulatory limits when this occurs.

**Step 3** – remove caustic for beneficial reuse, after complete ammonia recovery, the caustic may be dissolved to a required concentration for pumping into transport drums for use in other processes (e.g., neutralization of some acidic process). This recycling feature is preferable, eliminating a disposal stream by providing a beneficial use for the caustic. Alternatively, neutralize ready for disposal preparation in accordance with the following reactions.



Neutralizer may be selected from such reactants as HCl, H<sub>2</sub>SO<sub>4</sub>, HI, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub>, or others, so that metallic compounds become chlorides, sulfates, iodides, phosphates, or nitrates, respectively. Water is evaporated so that dry compound remains, which can be collected into 55 gallon drums for disposal as LLW. Note that Na<sub>2</sub>SO<sub>4</sub> does not dissolve in water and makes an ideal candidate for land fill disposal, compared to other compounds.

### **Chemistry Advantages**

When compared to water vapor processes, the AMANDA process takes advantage of four attributes relating to sodium conversion using a solvated solution:

1. The ionized sodium atom in solution can never return to its elemental state. If a pure solvated solution is allowed to evaporate, the sodium will finally react with the ammonia itself to produce sodamide (NaNH<sub>2</sub>), releasing a hydrogen atom in the process. At the end point of the evaporation, only sodamide will remain. Sodamide will react with water vapor in the air to release ammonia vapor and form sodium hydroxide. Concerns for unreacted residual elemental sodium are eliminated.
2. The solvated solution “slows down” the kinetics of the reactions, making process control much less complicated than one involving water vapor injection into a sodium environment. The sodium is dispersed throughout hundreds of gallons of ammonia, rather than being concentrated in one place. There are no localized pockets of sodium (localized sources of reaction heat, which in many cases is enough to cause sodium to melt).

- 3 The ammonia is a heat sink, instantly absorbing the energy release of any reactions. This energy supplies latent heat of evaporation, vaporizing (boiling) the ammonia. By exhausting the ammonia vapor to a heat exchanger (refrigeration technology), the temperature (and pressure/temperature range of ammonia) is controlled. Indeed, the process most often is completed at relatively low pressures. Condensation of water in "pockets" capable of sudden unpredictable flow resulting in contact (and reaction) with sodium, as could happen in a water-based process, is not possible with the solvated solution.
4. The ammonia environment is inert for most applications. Ammonia displaces inert covering gases (nitrogen or argon), then performs the same function. During sodium conversion, there is no buildup of scum, oxides or other screening or difficult to manage compounds, nor are there problems with oxygen intrusion. The sodium hydroxide simply falls out of the solvated solution and additional water is added to effect whatever concentration of sodium hydroxide is required prior to recovering the ammonia.



Figure 1. Color change is readily apparent here as solvated solution (sodium dissolved in anhydrous ammonia) is converted to caustic in seconds with titration by water.

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