What are Molten Salts?

What is Molten Salt? Molten Salt is a rather dreadful name for an otherwise useful catagory of materials & processes. The term "Molten Salt" is self-descriptive; it is melted salt(s). Another common name is Fused Salt(s). The simplest example of a molten salt would be to take sodium chloride ("table salt") and heat it to a red heat (greater than 801° C, or 1474° F)1 where it would melt into a liquid. This liquid is stable, has a heat capacity similar to water (by volume) and flows much like water does. The major differences are the obvious higher temperatures attainable in the molten salt state and when the salt solidifies (freezes) it contracts versus expanding like water. Thus, molten salt freezing in a pipe would not burst the pipe as water would.

Salts are simple, usually ionic (that is the chemical bonds are a simple ionic type) and stable compounds. The most common example of which is "table salt", or sodium chloride (NaCl). Both sodium and chlorine are notoriously reactive; sodium is one of the most electropositive substances (wants to lose an electron) & chlorine one of the most electronegative (wants to take an electron). These two opposite substances readily join to form stable sodium chloride via a strong ionic bond. The melting point of sodium chloride is 801° C (1474° F)₂, at which point it becomes a liquid, and thus a "molten salt".

Features of Molten Salts

Conducts Electricity

One of the interesting features of molten salts is their ability to conduct electricity. For example, solid sodium chloride (NaCl, or table salt) does not conduct electricity; it is an insulator. If NaCl is placed into water, the mutual attraction both sodium (Na) and chlorine (Cl) have for water molecules cause their bonds to break (dissolving) and form ions (charged atoms or molecules) within the water. These electrically charged ions can conduct electricity if there is a voltage potential (electric field).

To test this, place two electrodes in distilled water & using an ammeter, check to see if there is a current flow when a voltage is applied. There will be virtually no current flowing as water is a very poor conductor of electricity. Add a substance that will dissociate into ions (an "electrolyte"), such as table salt, and current will flow. Furthermore, this current will allow the transfer of ions (movement of ion charge 'packets') so that either the water will be dissociated into its component gases hydrogen and oxygen, or, depending upon the electrolyte, the some of the electrolyte (NaCl, in this case) may be dissociated instead, thereby releasing the gas chlorine; which is how most chlorine gas is produced (electricity is passed through concentrated salt water).

Molten salts conduct electricity the same way they do when they are dissolved in water; some of the salt molecules are dissociated into ions, which allows the ions to conduct electricity. The "Downs Cell" capitalizes on this conduction of electricity to produce virtually all of the metallic sodium required by industry. Electricity is run through molten sodium chloride (with a little calcium chloride salt added to lower the melting point of the sodium chloride). At one terminal chlorine gas is released (the anode) and at the other (the cathode) liquid sodium.

Using Electricity to Dissociate (Decompose) Chemicals

The principle of running electricity through molten salts has been around for quite some time. In fact, the first commercial application of electrolytic molten salt technology was the development of the Hall-Héroult electrolytic process for producing aluminum metal in 1886, but the British chemist Sir Humphry Davy had performed the basic experiment in 1809!<u>3</u> So, as you can see, molten salt technology has been around for almost 200 years.

What is Molten Salt Technology?

Molten salt technology is a catch-all phrase that include some very diverse technologies; electrochemistry, heat transfer, chemical oxidation/reduction baths, and nuclear reactors. All of these technologies are linked by the general characteristics of molten salts:

- Can function as solvents
- Have good heat transfer characteristics (heat capacity)
- Function like a fluid (like water)
- Can attain very high temperatures (red heat; $> 700^{\circ}$ C)
- Can conduct electricity
- Some molten salts have chemical catalytic properties

Molten Salt Heat Transfer - Solar Power Tower

Molten salts have been used in many industries as a high temperature heat transfer medium. The 'highest profile' use of molten salts in this regard is the Solar Power Tower near Dagget, California (excuse the pun). It uses a Sodium Nitrite/Nitrate mixture to absorb and store the sun's heat from the focus of many mirrors in the desert upon a central tower. The heat from the salt is then transfered via a heat exchanger to produce steam to drive a conventional steam turbine and generator to produce electricity from the sun for Southern California.<u>3a</u>

Molten Salt (Pyroprocessing) of Non-Ferrous Metals

Molten salts are also used to produce most non-ferrous metals (non-iron like metals; e.g., aluminum, titanium, etc.). The most notable and oldest use was the previously mentioned production of aluminum via electrolytic decomposition of alumina (aluminum oxide; Al_2O_3). A non-electrical method of using

molten salts to produce metals is used to produce titanium. Titanium oxide from various ores is reacted with chlorine and carbon (usually in the form of petroleum coke) to form titanium tetrachloride ($TiCl_4$),

which is a salt of titanium. This salt is melted and boiled off so as to distill and purify the TiCl₄. It can

then be contacted with sodium (produced via the previously mentioned molten salt Down's Cell) or magnesium metal in the Hunter or Kroll process (respectively) to produce titanium sponge and sodium chloride (NaCl) or magnesium chloride (MgCl₂). The titanium sponge is a raw material in the

fabrication of finished titanium metal products.

Molten Salt Salt Electrolytics - Fuel Cells

Molten salts are also used in Fuel Cells. While there are many different type currently being researched, the usual characteristics is to employ a mixture of various salt carbonates (e.g., Na₂CO₃, sodium

carbonate & other carbonates of lithium, potassium, etc.) as the electrolyte of a battery called a fuel cell. The advantage of this type of fuel cell is its ability to use carbon containing fuels (methanol, gasoline, etc.) directly in the production of electricity. The disadvantage is these molten salts corrode metal very easily. Lifetimes of the electrodes is still a problem area.

Molten salts are currently used commercially to strip metal clean of impurities. This simple process utilizes the high temperature and catalytic and oxidative properties of Sodium Nitrite/Nitrate (NaNO₂/NaNO₃) salts. For example, Whirlpool (the appliance manufacturer) uses a molten salt bath of sodium nitrite/nitrate salts to clean the paint off of its appliances that failed quality control checks. The molten salt completely cleans the metal of all paints by thermally decomposing and oxidizing the paint into

carbon dioxide (CO₂) & water (H₂O) vapors. The stripped metal appliance can then be repainted.

Molten Salt Oxidation (MSO) - Coal Gasification

Molten salts have also been studied since the early 1900s to gasify coal in a process called Molten Salt Oxidation (MSO). The molten salt used is usually sodium carbonate heated above its melting point of 851° C (1564° F) to around 900° - 1000° C. At this temperature the red hot salt functions as a catalyst, fluid reacting bed, and heat transfer medium; all in one! The coal is flash pyrolyzed such that no tars or oils are produced. Steam is usually injected too so that the combination of coal's thermally decomposed higher organic molecules along with catalytically assisted carbon-steam reactions (i.e., $C + H_2O = CO + H_2O =$ H₂) produces mainly carbon monoxide (CO) and hydrogen (H₂) gases at atmospheric pressures. At higher pressures, there will be significant methane (CH_4) and higher hydrocarbons produced. Carbon monoxide (CO) and hydrogen (H_2) can be used directly as a fuel gas or as a synthesis gas to produce virtually any organic material. The most common use of synthesis gas however, is to produce Methanol (methyl alcohol - CH₃OH) which can also be used as a fuel, and is used in race cars, but is usually a raw material for the production of various organics (octane boosters, gasoline additives, plastics, chemicals, and drugs). Given the renewed interest in the so called "Hydrogen Economy", whereby hydrogen is used as a "carrier fuel" to provide energy portability and transmission, it is likely MSO will play a significant role in the production of hydrogen fuel for the Hydrogen Economy via the "water shift" reaction where the Synthesis gas (the mixture of CO and H₂ gases decribed above) is converted into nearly pure H₂ gas

by the following, catylized reaction:

$$CO + H_2O = CO_2 + H_2$$

The CO₂ can then be fairly easily removed via various reactions, as it is a mild acidic gas which can be combined with various alkaline substances [e.g., CaCO₃ (s) + H₂O + CO₂ = Ca(H2CO₃)₂ (aq)]. Generally, the more alkaline the substance the faster and more complete the reaction (absorbtion) of the CO₂. Thus, sodium hydroxide (i.e., "Drano", or Lye - NaOH) would work much better at absorbing the carbon dioxide. Another method to remove the CO₂ from the H₂ gas is via liquification (using pressure and lower temperatures) of the carbon dioxide gas which liquifies much easier than the hydrogen gas. The liquified CO₂ could then be resold for various industrial or food processes.

Molten salt gasification of coal has also been proposed for wastes, to include <u>garbage</u> (Municipal Solid Wastes - MSW).

Molten Salt Oxidation (MSO) - Chemical Weapons

In the mid-1950s Rockwell, Inc. conducted extensive tests of molten salts for the purpose of destroying chemical weapons. This was also called Molten Salt Oxidation (MSO --> good description at Lawrence Livermore National Lab's <u>Upadhye's MSO description</u>), and was a spin-off of the earlier coal gasification studies. Similar to the advantages of using molten sodium carbonate to gasify coal, MSO has the additional advantage of having large amounts of sodium in close proximity to the decomposing chemical weapons molecules. This is significant because chemical weapons usually contain large amounts of fluorine, sulfur and/or chlorine, all of which can form radicals which may cause the production of carcinogens such as dioxins. The long residence times of the chemical weapons in a molten salt bath, as compared to incineration, combined with the presence of large amounts of sodium allows the chlorine, sulfur, and fluorine radicals plenty of time to form stable, and safe, sodium compounds such as sodium sulfate (a laundry soap and food additive), sodium chloride (table salt), and sodium fluoride (an anti-cavity toothpaste ingredient). Although there were no significant technical obstacles to employing MSO for chemical weapons' destruction, widespread Molten Salt ignorance and inertia prevented its deployment.

Molten Salt Reactors (MSRs) - a type of Nuclear Reactor

The most interesting application of molten salt technology was the development of the Molten Salt (Nuclear) Reactor (MSR). Originally developed to power a deep penetration bomber for targets in the Soviet Union during the early Cold War (1946 - 1962)<u>4</u>, it is a remarkable, yet virtually unknown reactor. Part of the problem was the limited geographical experience of the MSR as both operating MSRs were built only at Oak Ridge National Laboratory (ORNL), near Knoxville, Tennessee, USA.

The first MSR was the 1954, 100-hour operation of the Aircraft Reactor Experiment (ARE) at ORNL<u>5</u>. Its sole purpose was to demonstate the then unheard of notion of operating a reactor at red heat (~750° C; ~1,550° F) with a molten fuel and coolant consisting of melted fluoride salts (sodium fluoride, NaF; zirconium fluoride, ZrF ₄; and UF₄ [enriched in ²³⁵U])<u>6</u>. The second MSR was a civilian power plant prototype, the Molten Salt Reactor Experiment (MSRE)<u>7</u>. Hugely successful, it was ignored by the US Atomic Energy Commission (US AEC), which had decided to favor the Liquid Metal Fast Breeder Reactor (LMFBR). The Director of ORNL, Dr. Alvin Weinberg, pushed for the MSR, but was fired for his efforts <u>8</u>.

The notable features of this reactor are:

• Meltdown proof

What is Molten Salt & Its Technology?

- Does not produce weapons grade plutonium
- Has inherent non-proliferation features
- Thousands of years of energy
- Simplified fuel cycle (no fuel elements nor reprocessing required)
- Its wastes are simpler and less toxic than current nuclear wastes
 - o Only hundreds of years of storage versus thousands for the current wastes
 - Can completely destroy military plutonium
 - Can burn the existing wastes (spent fuel)!
- Higher thermal efficiencies (operates at a "Red Heat"; ~700° C [1,260° F])

References

1. Page B-137, <u>CRC Handbook of Chemistry and Physics</u>, 53rd Ed.

2. Ibid.

3. Britannica CD 97 search for "aluminum" AND "Davy".

3a. For more information on the use of molten salt for heat transfer and storage visit <u>Sandia National</u> <u>Laboratory's web site</u> at: (http://www.sandia.gov/Renewable_Energy/solarthermal/NSTTF/salt.htm)

4. Pages 15 - 20, subject listing "Aircraft Nuclear Propulsion (ANP) Program", in book, "<u>THE ATOMIC</u> <u>ENERGY DESKBOOK</u>", John F. Hogerton (1963).

5. R.C. Briant et al., Nuclear Science and Engineering, Vol. 2, No. 6, 795 - 853 (1957).

6. Page 677 of book, Fluid Fuel Reactors, James A. Lane, H.G. MacPherson, & Frank Maslan (1958).

7. Pages 377 - 378, "The Molten Salt Adventure", by H.G. MacPherson, NUCLEAR SCIENCE AND ENGINEERING, Vol. 90, pgs 374-380 (1985).

8. Pages 198 - 200, "<u>The First Nuclear Era : The Life and Times of a Technological Fixer</u>", by Alvin Martin Weinberg (1994).

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