SAGUACHESOLAR

Characteristics of Nitrate Salts

Sodium nitrate ($NaNO_3$) is a white, odorless, solid, prilled or crystalline chemical compound used primarily as an ingredient in fertilizers. Although it is classified as an oxidizing agent, the substance is non-combustible. In the dry chemical form, contact with combustible material will not cause spontaneous ignition, however, the substance will enhance an existing fire (but not cause an explosion). The chemical will not be stored on-site for more than a few months as a dry solid before being melted and stored as a liquid inside the hot and cold storage tanks.

The substance is stable under normal storage and temperature conditions, such as will exist while the material is temporarily stored on-site. The solid material begins to decompose thermally at about 380°C (716°F) as a reversible equilibrium reaction to sodium nitrite and sodium oxide (described further in detail below). This process does not present a concern for emissions as the equilibrium occurs in the presence of air. Additionally, the material will be segregated from other materials during temporary storage on-site. In the event of a fire, the substance can be extinguished by spraying with water.

Note that if the system salt flow stops, or anything else goes wrong with the facility operation, emergency off-pointing procedures will be implemented for the mirrors. There are backup generators in place so that no matter what, the mirrors can be turned away from the receiver.

The salt is hydrophilic and tends to collect atmospheric moisture and solidify into blocks. Physical handling of the salt is not expected to cause salt particles to become airborne. Inhalation of salt particles will likely irritate the respiratory tract, and symptoms may include coughing. It may cause irritation if in contact with wet skin. During the salt melting process, the dry crystalline material will be loaded into a crusher to reduce any sizable solids prior to blending with potassium nitrate and introduction to the melter. This process will be conducted in a negative ventilation enclosure, exhausted through a baghouse filter to prevent salt particles from becoming airborne and being released to the atmosphere.

When exposed to soil and water, the chemical dissociates into sodium and nitrate ions. Nitrates may be absorbed by plants and converted into organic nitrogen, whereas sodium binds to clay particles in the soil. Thus, it represents virtually no hazard to the environment if released into the environment. In high concentrations, the chemical may be toxic to marine life. As there are no bodies of water nearby, and the salt will solidify upon exposure to ambient conditions, the risk to the environment is minimal over the life of the project.

Potassium nitrate (KNO_3) is also a white, odorless, solid or crystalline chemical compound used primarily as an ingredient in fertilizers. Although it is classified as an oxidizing agent, the substance is non-combustible. Similar to sodium nitrate, contact with combustible material will not cause spontaneous ignition, however, the substance will enhance an existing fire. In the event of a fire, the substance can also be extinguished by spraying with water.

Like sodium nitrate, potassium nitrate is stable under normal storage and temperature conditions. The solid material begins to decompose thermally at about 400°C (752°F) as a reversible equilibrium reaction to potassium nitrite and potassium oxide (described further in detail below). It is likewise an irritant if inhaled or comes in contact with wet skin. It can also be toxic to fish in high concentrations, however, when exposed to soil and water, the chemical dissociates into potassium and nitrate ions, and the nitrates are absorbed by plants and converted into organic nitrogen, whereas potassium binds to clay particles in the soil. The chemicals are not considered to be a carcinogenic risk.

Experience from the Solar Two facility near Barstow, CA in late 1990's has demonstrated that the nitrate salts, if leaked from the plant's system in liquid form, almost immediately crystallize at atmospheric temperatures and present minimal danger to equipment or personnel. The plant did experience a few small leaks during its 3-year operating life, and according to eye-witness reports, material that came in contact with vehicles was simply washed off with no damage to the vehicle. At the end of the Solar Two plant's operating life, the nitrate salts were re-solidified and sold to local farmers for fertilizer.

Much research has been conducted on the nitrate salts, primarily by Sandia National Laboratories (SNL). When brought into contact with water or with fuels, such as gasoline or diesel fuel, the salts are non-reactive. The material will not

break down chemically over the expected 30-year life of the plant under the range of operating temperatures from 550°F to 1,050°F. (The liquid compound would begin to decompose chemically at higher temperatures as described further below.)

Pratt & Whitney Rocketdyne (PWR) test data indicates that the nitrate ($-NO_3$) salt starts a reversible reaction and turns into nitrites ($-NO_2$) at 1,170°F (120°F above normal operating temp) after approximately 2 minutes. When the salt cools back to 1,050°F, the nitrite fraction reverts back to its original nitrate state. The Solar Two experience and SNL testing support these results. Over the 30+ year life of the salt, there will be some fraction that will remain in the nitrite state of the equilibrium reaction and will have limited, if any, impact on the thermal capacity of the salt. Irreversible salt decomposition (into other chemicals) will only occur for sodium and potassium nitrate salts at much higher temperatures, but will not result in danger of explosion.

A small fraction of salt is provisioned into storage system to account for any potential loss through leakage in its lifetime. No addition of salt is expected for the system over its operating lifetime.

Some incorrect information exists in the literature about the decomposition point of molten salts, including sodium nitrate and potassium nitrate. In older literature, researchers may have observed oxygen evolution from the equilibration of nitrates and nitrites or may have observed some gas from the decomposition of magnesium nitrate and mistakenly attributed this to salt decomposition. Decomposition temperatures of sodium nitrate and potassium nitrate are described below in more detail and are much higher than the plant operating temperature. As further evidence of the stability of sodium nitrate and potassium nitrate, laboratory tests at SNL and periodic analysis of the salt during Solar Two operations did not indicate any long-term decomposition of the sodium nitrate/potassium nitrate salt mixture at 1,050°F. Note that the molten salt exiting the receiver will not exceed this temperature. The flow speed of the molten salt is controlled so that the salt temperature exiting the receiver is held constant.

The mixture of sodium nitrate and potassium nitrate proposed for this project was employed and proven at Solar Two. It is documented in the Solar Two final report that, among many salt mixtures considered, this mixture has the highest

thermal stability. At the temperature range for this application of 550°F to 1,050°F, the specified salt mixture exists in equilibrium between the nitrate and nitrite form of the salt as shown below:

$$NaNO_3 \leftrightarrows NaNO_2 + \tfrac{1}{2}O_2$$
$$KNO_3 \leftrightarrows KNO_2 + \tfrac{1}{2}O_2$$

Over time, the concentration of nitrite increases. This characteristic is anticipated and does not adversely affect the performance of the salt (as documented in the Solar Two final report.) At the maximum operating temperature of 1,075°F, there would be some degradation of the nitrite form of the salt as shown in the following equation:

$$5NaNO_2 \leftrightarrows 3NaNO_3 + Na_2O + N_2$$

This process, however, is very slow. It would take a much higher operating temperature, approaching 1,500°F, for nitrogen (N_2) to evolve so rapidly that the molten salt would appear to boil. In laboratory analyses, decomposition ceases as soon as the source of heat is removed, indicating that the decomposition reaction is endothermic. For sodium nitrate/nitrite, irreversible decomposition would occur closer to 1,470°F (800°C). The decomposition temperature for potassium nitrate/nitrite would be even higher. In summary, irreversible salt degradation and gas evolution (after the initial conditioning of the salt) is not expected throughout the operating life of the salt.

The molten salt storage tanks will be open to the atmosphere (through vents, described below) and a nitrogen "blanket" atmosphere will not be needed. As described above, the nitrate/nitrite equilibrium is anticipated as a normal process in the course of operation. The use of nitrogen cover gas would push the chemical equilibrium toward the formation of more nitrites.

The molten salt storage tanks are open to the atmosphere through vents designed in accordance with relevant codes; therefore, no pressure relief valve is required for these tanks. However, pressurized salt-circulating piping (to and from the receiver and to and from the steam generator system), and associated heat exchanger vessels, will be protected against over-pressurization by safety-relief valves designed in accordance with relevant codes (e.g., ASME). The highest

pressure developed in the system is about 700 psig at the discharge of the cold salt pumps. Numerous high-point vents are installed in order to expel air from the system when being filled (and drained). Air from these high-point piping vents is routed to the air space in the cold molten salt storage tank.

Prevention of Catastrophic Events

In order for an explosion to occur, a strong oxidizer would require a strong reducing agent in precise proportions. The mixture would immediately produce a violent exothermic reaction and the rapid release of gases, resulting in an explosion.

While the salts are stored for a short time on-site as a solid, there will not be any reducing agents on-site during that time to react with the nitrate salts. Additionally, the salts will be segregated from all other materials and stored in a separate covered storage enclosure until melted and loaded into the permanent storage tanks. Once the salt is loaded into the tanks, and for the 30 year duration of plant operations, the salt will be contained in a closed system without the ability to interact with any substance other than air. As such, a molten salt explosion would be chemically impossible.

There is a large recessed area around the tanks that is designed to contain the entire contents of the salt in the event of a catastrophic rupture of either tank. Moreover, the salt solidifies once exposed to the atmosphere, limiting the extent to which the salt could flow. If there were a spill, the risk of fire would be extremely low since nothing flammable will be stored in the retention basin. In the remote chance that there was a fire in the vicinity of the salts, simply spraying with water would extinguish the fire. Additionally, the standard fire protection systems and equipment associated with a power plant that are required by NFPA will be present, including a dedicated reserve of water for fire protection, electric motor-driven and backup diesel-driven fire pumps, fire hydrants, extinguishers, and fogging systems. The plant will also have a dedicated fire monitoring and alarm system that will be located in the Operations and Control Room. Operators will monitor the plant on a 24 hour per day basis over the life of the plant – even when shut-down – to ensure prompt action in the event a fire is detected.