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THE KNOWN UNKNOWNS OF MOLTEN SALT REACTORS

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ABSTRACT – Molten Salt Reactors (MSRs) are a class of reactors in which a molten salt performs a significant function in the core. These reactors are at a point of high technological maturity, they have many advantages and past operating experience, and deserve re-examination. From the beginning, structural material integrity in molten salt mixtures has been a concern, with corrosion, stress corrosion cracking, and helium embrittlement among the primary challenges. Structural material performance for the MSR are still a concern, though progress has been made.

Introduction

History has taught us that necessity is the mother of invention. The ever-growing global need for reliable electricity generation, and the need to mitigate the risks of burning fossil fuels has renewed interest in nuclear power in all its forms. The success of water-cooled nuclear power reactors in the 1960s and 70s hampered the development of many promising alternatives, and the waves of social acceptance in the decades since have left little investor appetite for unproven technologies. New reactor concepts must improve on existing technology: they should be more sustainable, more economic, while remaining safe, reliable, and resistant to nuclear proliferation and terrorist attack. The molten salt reactor (MSR) concept is attractive in this context.

1. The Birth and Development of an Idea

The perceived need for a nuclear-powered aircraft in the 1940s gave birth to the MSR concept. An MSR is a fission reactor in which the coolant, or even the fuel itself, is a molten salt mixture [1]. Between 1950 and 1976 a large MSR development program was conducted in the United States at Oak Ridge National Laboratory (ORNL): two test reactors were successfully operated; the design of a 1000-MW(e) breeder reactor was completed; and plans were developed to construct a demonstration reactor[2], [3]. For higher thermodynamic efficiency, MSRs run at higher temperatures than water-cooled reactors, while staying at low vapor pressure [1]. Like other liquid fuel reactors considered at the time (uranyl sulfate in heavy-water reactors and liquid-metal fuel reactors), molten-salt reactors had the advantage of simplified fuel reprocessing, which made it effective as a breeder reactor.

However, just as the MSR program was shutting down, a new focus on non-proliferation in the late 1970s resulted in a conceptual design for a so-called “denatured” molten-salt reactor (DMSR) that differed widely from the breeder design [4].Denaturedfuel is not suitable for weapons use and cannot be easily made so; low enriched uranium with less than 20% ^{235}U content is an example. Most notably, while the breeder reactor required an online reprocessing facility, the “denatured” MSR would run on an initial charge of fissile and fertile material that would be periodically topped up with denatured ^{235}U. Spent fuel would not be removed until the end of reactor life. This form of MSR has advantages as alternatives to current water-cooled reactor designs are sought, including:

- Low-pressure coolant,
- Good chemical stability, even when exposed to air or water,
- Prompt negative temperature coefficient of reactivity,
- Good neutron economy due to the lack of cladding,
- Passive cooling of drained fuel salt,
- Xenon removal through gas sparging,
- High fuel burnup,
- Less nuclear waste, and
- High thermal efficiency.

The operational experience for these and other MSRs comes from the single fluid 8 MW (th) Molten Salt Reactor Experiment (MSRE), which operated successfully during the period of 1965 to 1969. The limited experience obtained during the previous Aircraft Reactor Experiment (ARE) was incorporated in the MSRE. The MSRE fuel salt was a mixture of uranium, lithium-7, beryllium, and zirconium fluorides. Unclad graphite served as a moderator. All other parts of the system that contacted the salt were made from the nickel-base alloy HASTELLOY® N (17% Mo, 7% Cr, 5% Fe, balance Ni), which was specially developed for use with molten fluorides during the aircraft reactor program [5]. After the MSR experiment, ORNL concluded that there were many areas of molten-salt technology requiring further development before proceeding from this small non-breeding experiment to a safe, reliable and economic full-scale power reactor. Problem areas included issues with structural material integrity, tritium control methods, reactor equipment and systems, maintenance techniques, safety technology, and MSR codes and standards [3].

2. Structural Material Integrity Issues

In regards to material integrity issues, the operation of the MSRE revealed two potential problem areas that would have to be addressed for longer lived reactors:

- Grain boundaries of the Hastelloy N directly exposed to the fuel salt were shown to have been embrittled to depths of 0.15-0.25 mm. Studies showed the embrittlement to be associated with the presence of tellurium (a sulfur-like fission product) in grain boundaries that intersected with the salt-exposed surfaces, and
- Helium production from ^{10}B and directly from Ni by a two-step reaction was found to have reduced the creep ductility of the Hastelloy N, known as helium embrittlement.

Because the depth of cracking observed due to Te in the MSRE would not be acceptable when extrapolated to the 30-year design life of an MSR, solutions to this problem were explored [6]. It was found that high-Cr alloys were resistant to intergranular attack by Te, but were more susceptible to general corrosion. Additions of Nb to Hastelloy N improved resistance to intergranular cracking by Te [7], [8]. Furthermore, experimental results showed that controlling the

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molten salt oxidation potential had dramatic effects on the extent of cracking [9]. However, Nb-modified alloys are likely not useful at operating temperatures much above 650 °C due to a low creep rupture strain [7].

The addition of Ti to HASTELLOY® N alloy appeared very beneficial at suppressing helium embrittlement, and was followed by the development of Ti-modified alloys. 2%-Ti-modified alloy was found very resistant to irradiation embrittlement at temperatures up to 700 °C and exhibited acceptable mechanical properties [7]. However, it was found that Ti was ineffective in preventing intergranular embrittlement by Te and, it also destroyed the beneficial effects of Nb when both elements were present [7]. Recently, Russian teams have suggested that an addition of 0.1% Mn in Nb modified Hastelloy N would reduce Te grain boundary embrittlement [10], [11].

For austenitic stainless steels, which are resistant to intergranular attack by Te, irradiation embrittlement can be mitigated by a fine dispersion of precipitated carbide particles: the helium atoms are then trapped at the matrix/carbide interfaces. Similar effects will show in Ni-base alloys, provided an adequate microstructure is obtained [12]. However, high-Cr alloys do not possess the same corrosion resistance in molten-fluoride systems that they have in water and air. In fact, chromium oxides readily dissolve in molten-fluoride salts, and Cr can be oxidized by reaction with UF_4, which increases the general corrosion rate of these alloys above that of low chromium Hastelloy N [14]. Previous experiments with molten-salt test loops have shown that the corrosion of Cr and its mass transfer from hot to cold regions, where it deposits, provides a mechanism for continued attack [15].

Temperature-dependent corrosion of this type is particularly applicable to high-temperature reactor systems, in which large temperature differences are found [4], [16], and [17].

2. Conclusions

The bottom line is that any alloy chosen for a new molten-salt reactor would have to be demonstrated to have acceptable resistance to general corrosion, intergranular attack by Te, and He embrittlement. Aside from these considerations, any other candidate material such as C-C composites, SiC-SiC composites, new Ni-based alloys and insulated low-alloy steels, will need to be fully qualified before its use in a MSR.

Another complication for the molten salt reactor is the thermal incompatibility of molten salts and steam systems: most molten salts freeze at temperatures above the critical point of water [18]. If a molten salt reactor is to be paired with a water Rankine cycle, it will have to be demonstrated that the combination does not lead to complications under all postulated conditions, including leakage into the fuel salt.

MSRs are a promising technology, with a firm technology base, and the need of alternatives to fossil fuels for energy generation is undeniable. Deployment of efficient, reliable and safe MSRs does require considerable R&D work, but it may well be worth the effort, as it could play an important role for the ultimate sustainability for our global society.

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