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Original Article

Transfer characteristics of a lithium chloride–potassium chloride molten salt

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ABSTRACT

Pyroprocessing is an alternative method of reprocessing spent fuel, usually involving the dissolving spent fuel in a molten salt media. The National Nuclear Laboratory designed, built, and commissioned a molten salt dynamics rig to investigate the transfer characteristics of molten lithium chloride–potassium chloride eutectic salt. The efficacy and flow characteristics of a high-temperature centrifugal pump and argon gas lift were obtained for pumping the molten salt at temperatures up to 500°C. The rig design proved suitable on an industrial scale and transfer methods appropriate for use in future molten salt systems. Corrosion within the rig was managed, and melting techniques were optimized to reduce stresses on the rig. The results obtained improve the understanding of molten salt transport dynamics, materials, and engineering design issues and support the industrialization of molten salts pyroprocessing.

1. Introduction

Electrometallurgical processing ("pyroprocessing") is a dry, high-temperature alternative method of reprocessing spent fuel, which does not require the use of solvent extraction and its associated chemicals. Pyroprocessing typically involves the dissolution of spent fuel into a molten salt media, for example, lithium chloride–potassium chloride eutectic (LKE) salt [1]. Uranium is electrochemically separated using a solid cathode (typically steel or graphite), and plutonium and transuranics are separated using a liquid cadmium cathode. Advantages of molten salt reprocessing compared to that of aqueous reprocessing include lower quantities of waste produced, inherent actinide partitioning, good nonproliferation characteristics, and better criticality margin (no water phase) [2]. In addition, the metal products of pyroprocessing could be utilized to close the nuclear fuel cycle, e.g., the metal fuel is produced from pyroprocessing of spent oxide fuel, and metal-fueled fast reactors burn this metal fuel and then the metal fuel undergoes pyroprocessing again, creating the closed cycle.

Molten salts have a variety of uses other than pyroprocessing, including molten salt reactors and molten salt solar power towers. Most molten salt applications still rely on pumps with significant moving parts, e.g., high-temperature centrifugal pumps [3], as these technologies are well developed and well understood. However, while handling radioactive fluids, two key issues are maintaining containment and preventing dose exposure for workers. Centrifugal pumps have significant disadvantages in this area, namely maintenance of moving parts, lubrication leaks and maintaining seals to prevent the spread of contamination, and back diffusion of radioactive gases [3]. In addition, when working with molten salts, maintaining cooling and managing thermal expansion must be addressed.

One solution commonly used in aqueous reprocessing is use of no-moving-part fluidic devices, e.g., reverse flow diverters (RFDs), vacuum lifts, air lifts, double diode pumps, and steam/air/water ejectors [4–6]. These pump devices address many issues around containment and maintenance but often at a sacrifice of efficiency.

Examples of no-moving-parts pumping technologies that have been tested in molten salt applications include vacuum pumps [7], suction pumps, [8,9] and vibrating pipe pumps [10].

Other no-moving-parts pumping technologies worth mentioning are electromagnetic (EM) or magneto-hydrodynamic pumps. These work through application of a strong magnetic field and electrical current to a conducting fluid in a channel, giving rise to an EM force in the fluid, causing it to move through the

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channel. EM pumps were used in nonnuclear applications such as pumping seawater, liquid metal reactors, and suggested for use in molten salt high-temperature reactors. The advantages of EM pumps include their simplicity and high power density but disadvantages include the need for good thermal insulation or cooling to protect permanent magnets [11].

2. Materials and methods

The National Nuclear Laboratory (NNL), at that time a part of British Nuclear Fuels Ltd, designed, built, and commissioned a molten salt dynamics rig (MSDR) during 2001–2004 to investigate technologies for pumping molten LKE salt. The approach taken for the MSDR was to select pumping technologies that were well understood and used by the nuclear industry and to investigate their suitability for molten salts. Therefore, the pumps selected were a high-temperature centrifugal pump (standard off-the-shelf design, high flow rate), gas lift (no moving parts, low flow but reliable), and a reverse flow diverter (no moving parts, good flow rates and off-the-shelf design possible).

The MSDR was made up of two main vessels: pumping vessel V2002 and receipt vessel V2003, each with a capacity of 182 L. The LKE salt was pumped from V2002 to V2003 using one of the three pumping technologies, with the LKE then returning to V2002 via a gravity drain pipeline (see Figs. 1 and 2).

The vessels were constructed using 316 stainless steel with a vessel thickness of 6 mm. Electric heaters were placed on the outside vessel wall. These were encased by a layer of steel cladding, Rockwool mineral wool insulation, and finally an outer steel cladding. All piping was constructed using 316 stainless steel, wrapped with an electrical heating tape, and surrounded by layers of Rockwool mineral wool insulation.

As described previously, three pumping technologies were selected for testing.

A gas lift uses gas injected into a rising pipe to transport fluid against gravity, resulting in two-phase flow up the pipe. Different flow regimes (bubbles, slugs, churn, annular flow, etc.) occur at different gas and liquid flow rates. In the MSDR, argon gas was used to pump molten salt from V2002 to receipt vessel V2003, up a vertical pipeline with an inner diameter of 26.7 mm and length of approximately 4.2 m. Pressurized argon was introduced just above an elbow bend such that there was a 2.2 m head of molten salt above it. The argon line ran counter currently along the molten salt

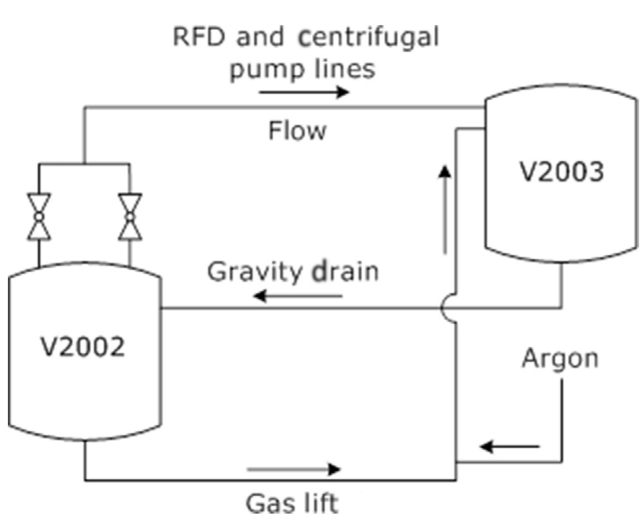

Fig. 1. Simplified schematic representation of the MSDR. MSDR, molten salt dynamics rig; RFD, reverse flow diverter.

transfer line to preheat the gas, and there was no sign of the argon cooling the salt during gas lift operation. Under normal operation conditions it was expected that the gas would pneumatically transport the melt in the slug flow regime of two-phase flow.

A vertical centrifugal pump (Rheinhütte GVSN 40/200A) with a 415 V three-phased Siemens motor was installed in V2002 to pump molten salt along a 4.2 m long pipe with six 90° bends to V2003. The rotor speed of the pump was controlled by a variable speed drive (Siemens Micromaster 440 Inverter Drive 0.37 kW, http://uk.rs-online.com/web/p/products/4660268/?grossPrice=Y), and the shaft was sealed with graphite gland packing. Nominal duty of the pump was 4.5 m^3/h with a 10 m head.

The RFD in the MSDR was submerged in V2002 along with a 10 L charge vessel and used argon gas. Molten salt was delivered to V2003. An RFD controller (Accentus Fluidtec Fluidic Pump Controller) controlled the argon supply to the suction and jet pumps, allowing drive time, drive pressure, and suction pressure to be set. Suction time was automatically controlled by the RFD software as a function of suction pressure to prevent fluid being sucked through the charge vessel up toward the jet pumps.

The rig was first commissioned with water in 2004, after which full molten salt trials ran from 2004 to 2006. Owing to organizational changes, the rig was put into a state of care and maintenance at the end of 2006 and was recommissioned in 2013 as part of the NNL's contribution to the REFINE project (a consortium of universities investigating molten salt reprocessing). After recommissioning, testing resumed, but a significant leak was discovered in 2015 during a gas lift pumping trial and operations halted. Investigations into the cause of the leak were carried out and the rig is now being decommissioned.

LKE was used as the salt medium as it has been identified for use in pyroprocessing flowsheets. The LKE supplied had a melting point of 357°C [12], a solid density of 2200 kg/m^3, and a liquid melt density of around 1620 kg/m^3 at 500°C [13]. The substantial decrease in the salt density on melting required careful designing and testing of the rig heating process. Salt melting started and progressed from free surfaces only (i.e., top down) to prevent the failure of components from thermal expansion of salt and subsequent pressurization.

The LKE salt was supplied in the form of solid, cylindrical slugs weighing approximately 1.3 kg each, at a purity of 99.99% anhydrous LiCl/KCl eutectic (LiCl 44 %w/w). The total salt inventory of the system was 115.6 kg or 69.2 L at 415°C.

LKE salt is hygroscopic in nature and readily deliquesces (absorbs moisture from the air and dissolves in it). This concentrated chloride salt solution is highly corrosive to stainless steel and carbon in the presence of oxygen and/or water. Therefore, controlling oxygen and water content was critical during all phases of rig operation. An argon-inerting and -purging blanket was used to prevent air and moisture ingress (resulting in an internal conditions of less than 500 ppm oxygen and 150 ppm water), controlled through a panel of control valves, regulators, relief values, and instrumentation connected to the rig.

Precautions also were taken while adding salt to the rig to maintain an inert atmosphere. Salt slugs were fed into a rig charging vessel V2001 via a sealed carrousel mechanism, designed to drop slug one at a time into the vessel minimizing the moisture entrainment. A total of 84 salt slugs were introduced into V2001 and melted over three batches of approximately 36 kg each. Initially, the vessel temperature was increased in a gradual stepwise manner until enough was known about the behavior of the system; subsequently, larger temperature increments were used to decrease the melting time. After each batch had been melted in the charging vessel, it was allowed to drain under gravity to the main pumping vessel V2002.

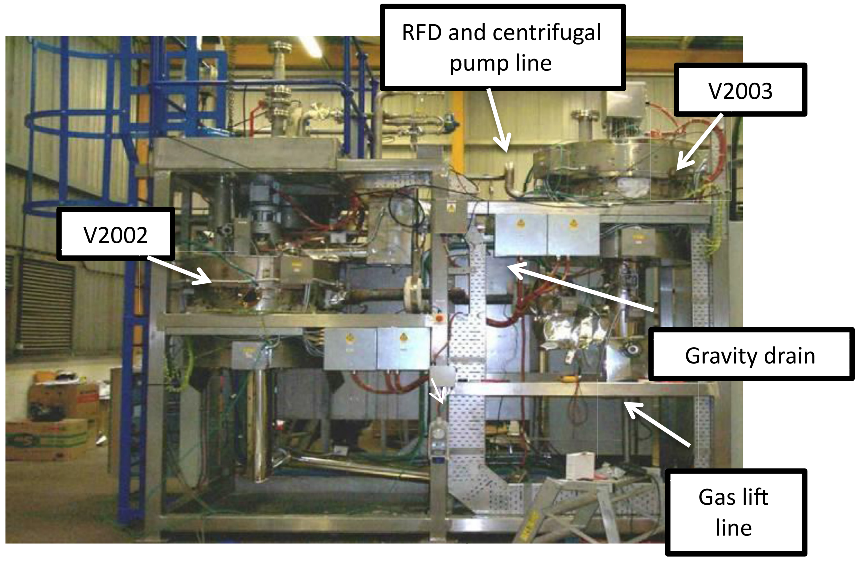

Fig. 2. Annotated picture of the MSDR. MSDR, molten salt dynamics rig; RFD, reverse flow diverter.

After the full inventory of salt was loaded into V2002, similar melting trials were carried out to optimize melting rate. The melting process for V2002 was as follows:

- The maximum power output to the vessel wrap heaters was limited to 55%, 35%, and 15% for the top, middle, and bottom wraps, respectively. Bottom heater power was conservatively limited to 15% to avoid hot spots and to provide some margin of safety during operations in absence of the operator, as any uncontrolled expansion of melting salt in this area could rupture the vessel.
- From ambient temperature, all heaters of V2002 were started simultaneously to preheat the vessel in a controlled manner, until middle and bottom salt sections reached temperatures of 300°C and 190°C, respectively.
- Middle and bottom heaters were turned off, and the top wrap heater temperature was increased up to about 425°C. The heat from the top wrap, possibly combined with the thermal inertia, brought the middle section of salt in V2002 to about 330°C.
- Next the set point of the middle wrap heater was gradually increased up to 450°C, while the top wrap was kept above 425°C. The bottom section of salt heated via salt convection only and the melt progressed from top to bottom.
- After the bottom section reached 390°C, the bottom wrap heater was switched back on. Total inventory melting was confirmed when the salt temperature at vessel base was 430°C for at least 5 minutes.

Flow rate was measured for water by collecting and weighing water over 120 s. Flow rate for molten salt was measured using pneumercators in vessels to measure level decreases and increases, as molten salt was transferred from one vessel to another. Argon flow rates were measured using flowmeters in the argon supply and control system.

During transfer operations, vessels V2002 and V2003 were kept at 490°C and transfer lines between 450 and 490°C.

3. Results

The MSDR ceased operations before sufficient molten salt pumping data could be obtained for the RFD, partly because flow rate of the RFD was dependent on more variables than the other pumping technologies (e.g., RFD suction pressure, drive pressure, drive time, and rest period between drive cycles). However, enough data were gathered to characterize the argon gas lift and centrifugal pump.

Water flow rate was measured by collecting and weighing water over 120 s. The experimental error was less than ±0.05 kg and ±1 s, giving an overall water flow rate error of less than 5%. The various argon flow rates were steady but measured with a poorer relative accuracy about ±0.025 m^3/h.

Experimental error for the molten salt flow rate was around 10%, as pneumercators were used to measure the molten salt level decreases and so flow rate from one vessel to another (calculated from difference in height of the molten salt measured in a vessel of known volume). A 1–2 mm error on the measured height of the melt was assumed; therefore, experimental accuracy was 5–10%.

Reproducibility of data between identical tests was better than ±10% supporting the above error estimates.

3.1. Argon gas lift water commissioning

During water commissioning trials, a linear relationship between argon flow rate and water flow rate was observed for an argon flow rate between 0.2–0.6 m^3/h (Fig. 3). Water flow rate then plateaued, reaching a maximum rate of 3.18 L/min despite increasing argon flow rate up to 1.6 m^3/h. Within an argon pressure range of 0.2–1.5 barg, water flow rate did not appear to be dependent on argon pressure, and very similar results were gathered. A minimum argon pressure of 0.13 barg was required to overcome the head of water.

These results provide a baseline to enable comparison of molten salts data.

3.2. Argon gas lift operating with molten salt

Enough data were collected to characterize the argon lift with molten LKE salt at 490°C. The volumetric flow rate was higher for salts than for water at similar argon pressure and did not appear sensitive to argon pressure for the range tested (0.2–1.8 barg), as with water. The minimum argon pressure required to start the transfer of molten salt was 0.3 barg at 500°C (for a 966 mm head), higher than that of water, as expected because of the higher density of the salt. Pressure oscillations in the argon lift line (0.2–0.35 barg

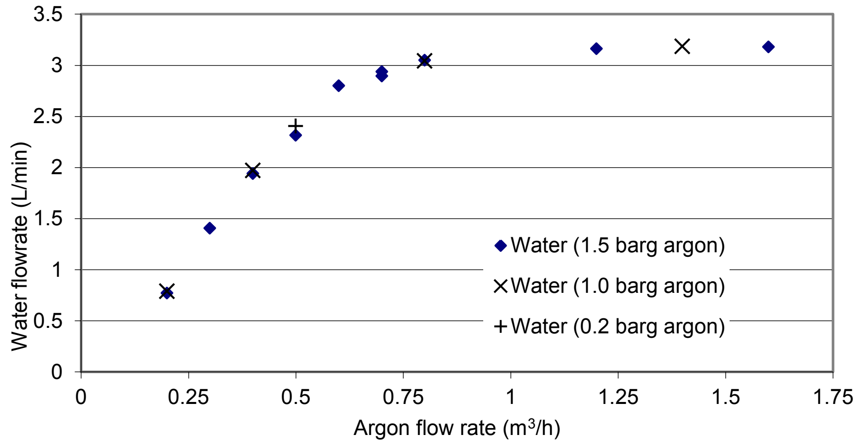

Fig. 3. Argon gas lift: water flow rate versus argon flow rate.

dependent on argon flow rate) suggest that most flow occurred in the slug flow regime.

The argon gas lift operated continuously for 64 h without any issues, proving the suitability of this pumping technology for long operating periods.

Volumetric flow rate at argon flow rates below 0.5 m^3/h was significantly higher (1.5-2x) for molten salt than water (Fig. 4). This was thought to be due to higher salt viscosity (around 4.64 cP at 400°C compared with 1 cP for water at 20°C [14]) resulting in better slug flow characteristics. As with water, LKE flow rate tended to a maximum despite increasing argon flow rate. It appeared that this viscosity effect also improved flow when LKE temperature was decreased from 500°C to 400°C, as the molten salt becomes more dense and viscous on cooling (although data were limited). Increased surface tension of LKE could also play a part (120 dyne/cm^2 compared to 70 dyne/cm^2 for water [14]), affecting pipe-wall effects.

The next stage was to investigate the effect of pressure head (measured as estimated head difference from top of melt in V2002 to argon injection point) (Fig. 5). It was expected that increased head difference resulting in increased pressure head would lead to higher flow rates, due to higher LKE density and viscosity. For a set argon pressure and varying argon flow rate and pressure head, melt flow rate increased linearly with head pressure up to a head difference of around 900 mm, before dipping. This suggests a change in two-phase flow regime at that point e.g., slug to churn flow. This dip effect was seen across a range of argon flow rates and corresponded to a 4–15% reduction in flow rate.

Two-phase gas–liquid flow rate is a nontrivial function of temperature, argon flow rate, argon pressure, and head of melt above argon injection point. It was not possible within the timeframe provided to obtain sufficient data to characterize flow regime because of the use of a slow “freeze valve” (to measure level decreases). This freeze valve is operated through heating and cooling a pipe section so that the salt froze or melted, controlling the flow rate. However, the freeze valve opening and closing cycle took several hours making flow characterization difficult. Experimental accuracy was about 5–15% mostly because of lack of accuracy of the variable area flowmeter for argon flow.

3.3. Centrifugal pump water commissioning

During water trials, water flow rate varied between 15.2 L/min (600 rpm, the minimum required for flow) and 66.2 L/min (1500 rpm, maximum power). Experimental accuracy was similar to the argon gas lift due to the water measurement method. The relationship between speed drive frequency and water flow rate was mostly linear up to 60 L/min, and the flow rate started to flatten off around 1200 rpm (65 L/min, or 3.9 m^3/h) (Fig. 6).

3.4. Centrifugal pump operating in molten salt

Enough data were collected to characterize the centrifugal pump with molten salts at 490°C. Flow rates for the molten salt were similar to water flow rates at ambient temperature. The pressure head increased linearly at a much steeper rate, which

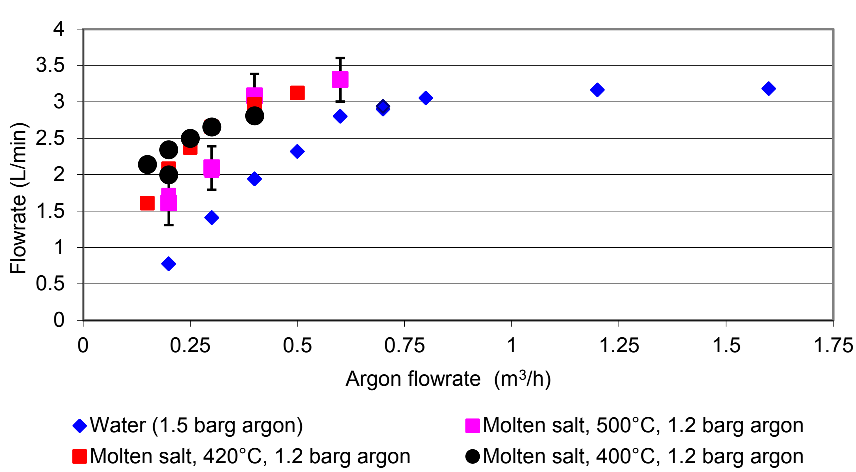

Fig. 4. Argon gas lift: temperature dependency of molten salt flow rate versus argon flow rate, water trial data included for comparison.

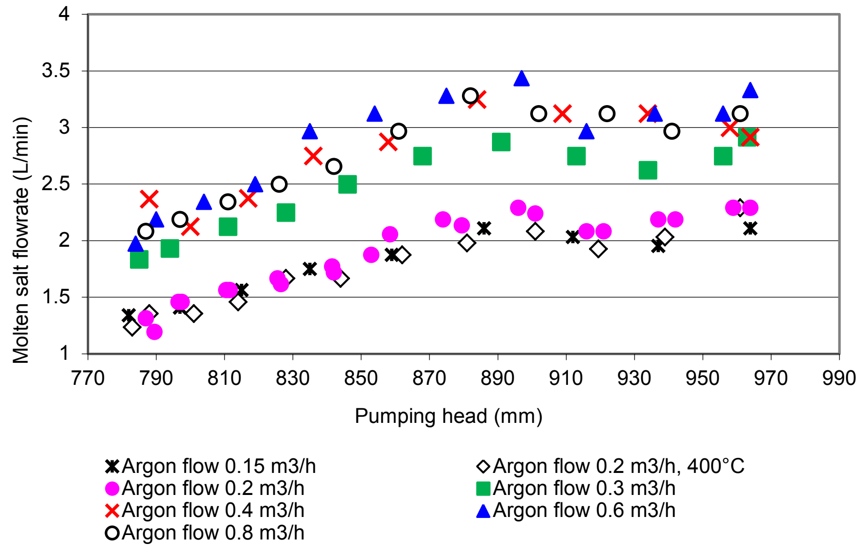

Fig. 5. Argon gas lift: effect of molten salt pressure head on flow rate (argon pressure 1.05 barg, temperature 500°C unless stated).

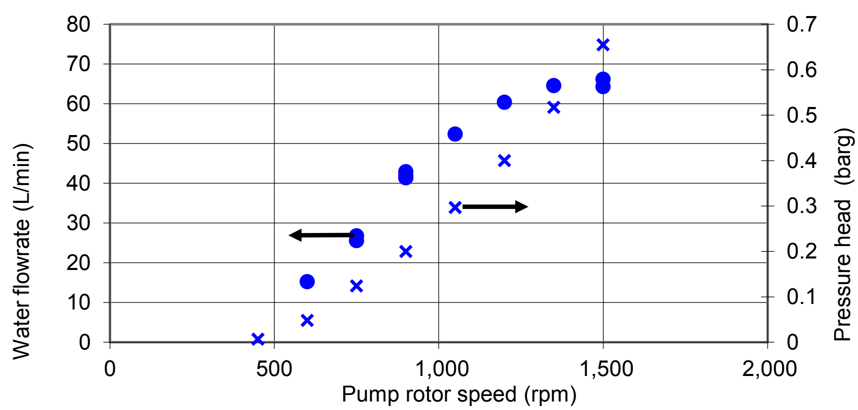

Fig. 6. Centrifugal pump: water transfer characteristic (in maximum flow conditions). Circles = water flow rate vs. rotor speed, crosses = pressure head vs. rotor speed.

would be expected due to the difference in fluid densities. Establishment of steady and sizeable flow occurred around 600–750 rpm, as with water (Fig. 7).

The centrifugal pump was operated continuously for 2 h at varying speeds. A maximum flow rate of 60 L/min was achieved at a rotor speed of 1350 rpm.

4. Discussion

As to be expected in water trials, the off-the-shelf 2.2 kW centrifugal pump was the most effective pumping method, reaching a maximum flow rate of 66.2 L/min. The argon gas lift pump was not effective, with a maximum flow rate of 3.2 L/min observed for 1.5 barg argon pressure.

While transferring molten salt, the centrifugal pump retained a similar effectiveness, achieving a maximum flow rate of 60 L/min at 490°C. With molten salt, the argon gas lift showed significant improvement compared to in water between argon flow rates of 0.15–0.6 m^3/h, trending to a maximum of around 3.3 L/min. The argon gas lift operated continuously for 60 h at 490°C without issues. In a nuclear installation, it is often not possible to maintain or replace parts due to high radiation fields and contamination. Hence, pumps with high reliability (e.g., no moving parts) are required. Therefore a high efficiency centrifugal pump could be used in pyroprocessing before the salt has been irradiated and a gas lift during reprocessing.

The MSDR was a challenging experimental work program but achieved its aim of demonstrating and quantifying the transfer characteristics of three techniques for transferring molten LKE on an industrial scale at 490°C (centrifugal pump, argon lift, and gravity transfer). Some data were gathered on the operation of the reverse flow diverter but not enough to fully characterize this technology with molten salt.

Flow characteristics of the argon gas lift and high-temperature centrifugal pump with molten LKE salt were obtained. Maximum flow rate for the argon gas lift was higher for LKE than water (for the same argon pressure and flow rate) due to viscosity effects. The argon gas lift also proved reliable over extended periods of over 60 h.

The corrosive nature of LKE salt was controlled via the argon blanket and purge system, such that when the rig was opened up for decommissioning no corrosion on inside surfaces could be seen.

Overall, the design proved suitable and transfer methods proved appropriate for use in future molten salt systems.

More testing and research is required before molten salts become a commercially viable alternative for nuclear fuel reprocessing. This data can be used to optimize transfer techniques, build new test rigs, and provide a baseline for alterative pumping

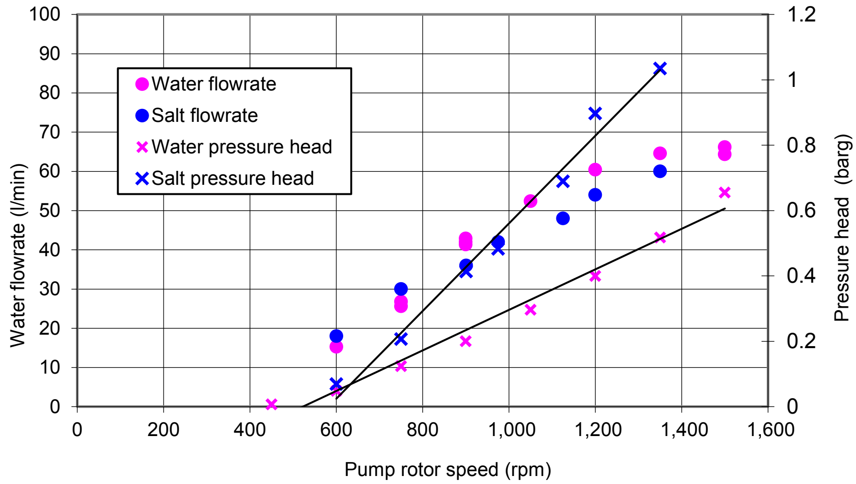

Fig. 7. Centrifugal pump: pump transfer characteristics for water and molten salt (in maximum flow conditions).

techniques. Paired with other NNL Molten Salt research, e.g., corrosion in molten salt environments, we can better understand the behavior and performance of molten salt systems.

Conflict of interest

We the authors wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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