

Chemistry and technology of Molten Salt Reactors – history and perspectives

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Abstract

Molten Salt Reactors represent one of promising future nuclear reactor concept included also in the Generation IV reactors family. This reactor type is distinguished by an extraordinarily close connection between the reactor physics and chemical technology, which is given by the specific features of the chemical form of fuel, representing by molten fluoride salt and circulating through the reactor core and also by the requirements of continuous ‘on-line’ reprocessing of the spent fuel. The history of Molten Salt Reactors reaches the period of fifties and sixties, when the first experimental Molten Salt Reactors were constructed and tested in ORNL (US). Several molten salt techniques dedicated to fresh molten salt fuel processing and spent fuel reprocessing were studied and developed in those days. Today, after nearly thirty years of discontinuance, a renewed interest in the Molten Salt Reactor technology is observed. Current experimental R&D activities in the area of Molten Salt Reactor technology are realized by a relatively small number of research institutions mainly in the EU, Russia and USA. The main effort is directed primarily to the development of separation processes suitable for the molten salt fuel processing and reprocessing technology. The techniques under development are molten salt/liquid metal extraction processes, electrochemical separation processes from the molten salt media, fused salt volatilization techniques and gas extraction from the molten salt medium.

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1. Introduction

Molten Salt Reactor (MSR) represents one of the promising high temperature nuclear reactor types for future generation of electricity and of heat for hydrogen production. It also could be used as transmuter to burn plutonium and other transuranium elements occurring in the spent nuclear fuel of nowadays-existing nuclear reactor types [1]. This seems to be of great importance because the spent fuel management strategy represents one of the most

serious problems, which should be appropriately solved for further sustainable development of nuclear power. Molten Salt Reactor is usually characterized as a non-classical nuclear reactor type due to a specific character of its fuel, which is liquid – constituted by a molten fluoride salt mixture circulating between a reactor core and a heat exchanger. The fission material (uranium and/or transuranium elements) is dissolved in carrier molten salt, which is also a heat-transferring agent.

The typical fuel of the Molten Salt Reactor working as the nuclear transmuter is a mixture of fluorides of plutonium and other transuranium elements (Np, Am, Cm), called usually as minor

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actinides, dissolved in the carrier fluoride salt. The other, very promising mode of Molten Salt Reactor operation is based on the use of ^{232}Th – ^{233}U fuel cycle with minimized production of long-lived nuclear waste in comparison to the ^{238}U – ^{239}Pu fuel cycle currently used in present reactor types. In this mode, the MSR works as a reactor-breeder producing own fissile material ^{233}U from fertile ^{232}Th . Essentially the main advantages of MSR comes out from the prerequisite, that this reactor type should be directly connected with the ‘on-line’ reprocessing of circulating liquid (molten salt) fuel. This fuel salt clean-up is necessary within a long run to keep the reactor in operation. As a matter of principle, it permits to clear away typical reactor poisons like xenon, krypton, lanthanides etc. and also the products of burned plutonium and transmuted minor actinides. On the other hand, the technologies of liquid transuranium molten salt fuel processing from the current spent fuel and of the on-line reprocessing of MSR fuel represent two killing points of the whole MSR technology, which have to be successfully solved before MSRs deployment in the future [1,2].

The history of Molten Salt Reactor technology reached nearly to the end of 1940s when Ed Betis and Ray Bryant from Oak Ridge National Laboratory (ORNL) began to study an ability to use nuclear reactors with liquid fuel based on molten fluoride salts. Later on, in the 1950s the military oriented Aircraft Nuclear Propulsion Program (ANP) was carried out in ORNL. The first small molten salt reactor mock-up was realized in 1953. However in 1954 the first real MSR was put in operation. The reactor, which reached the power of 2.5 MWt was just able to demonstrate successfully the MSR technology. Its primary fuel circuit was cooled by helium gas and the circulating fuel was comprised by NaF – ZrF_4 – UF_4 mixture with molar composition of 53–41–6. The reactor was operated about 100 MWh, maximal operating temperature of circulating fuel was 882 °C. At the end of 1950s, the motivation of use the MSRs for military use was lost. However, based on the promising results obtained during ANP, the development of the technology was consecutively oriented to the peaceful use and the work continued during the programs called Molten Salt Reactor Experiment (MSRE) in the 1960s and Molten Salt Breeder Reactor (MSBR) in the end of the 1960s and beginning of the 1970s. In those days, the main effort was focused to the demonstration of viability of the Molten Salt Reactor

and to the verification of the operation of the reactor. In the frame of MSRE, the experimental Molten Salt Reactor was realized and operated in the period 1965–1969. Initially the fuel for MSRE was constituted by ^7LiF – BeF_2 – ZrF_4 – UF_4 and the mixture of LiF – BeF_2 served simultaneously as the heat-transferring agent. In 1968, the original ^{235}U was extracted from the fuel salt and later replaced by ^{233}U . Also the composition of carrier fuel salt was changed and the new fuel salt was composed only from ^7LiF – BeF_2 – UF_4 . (The reason of isotope ^7Li use was to prevent the undesirable tritium production from ^6Li .) The moderator of the reactor was graphite; structural material of MSRE was nickel alloy INOR-8 (later called Hastelloy-N), the coolant of secondary circuit was LiF – BeF_2 eutectic. The power of MSRE was nearly 8 MWt and the working temperatures in the region of 600 °C [3–6].

2. Chemistry and chemical technology of MSR

The MSR fuel cycle chemistry was studied intensively during the MSRE, the liquid fuels for MSR were processed, however the MSR spent fuel reprocessing was never fully realized either in a pilot scale. For all that, considerable effort was carried out in radiochemical laboratory research to develop separation processes for uranium, protactinium and rare earth elements from the carrier molten salt. Also the basic flow-sheeting work was done during the MSBR program to design the main principles of MSBR spent fuel on-line reprocessing.

Nowadays, based on the new requirements of sustainable development of nuclear power, the MSR technology is under revival of interest in the frame of the development of advanced nuclear reactor types. Chiefly ‘Generation IV International Forum’ constituted by several most industrialized countries supports this renascent research and development. However, it is necessary to realize that the knowledge and experience of the Molten Salt Reactor technology is not well proportioned. Whereas the knowledge of the MSR performance is quite comprehensive, the MSR fuel cycle technology, including the ‘on-line’ reprocessing represents one of the poorest developed and verified areas. On the other hand, this area is experimentally studied at several workplaces at present.

The fuel cycle technologies of Molten Salt Reactors can be partially different depending on the type of used fuel in the reactor. Whilst the fuel processing for the MSR working as a transmuter (Molten Salt

Transmutation Reactor – MSTR) represents several processes and technologies of spent nuclear fuel partitioning, the preparation of liquid fuel for MSR working under ^{232}Th – ^{233}U cycle is different and much more easier. Of the specific category is the on-line reprocessing of MSR circulating fuel salt, which has to be done continuously and which is in principle similar for both types of MSRs.

The final part of fuel processing technology should be placed in the reactor site and tightly attached to the ‘on-line’ reprocessing, because the refilling of the fresh fuel into the reactor has to be carried out in connection with the removal of the burned out fuel and fission products from the primary fuel circuit (see Fig. 1).

The chemical separation (partitioning) technologies, which are often discussed in the frame of MSR (MSTR) fuel cycle and which have a connection to the general molten salt chemistry are mainly:

- Fluoride volatilization techniques
- Electrochemical separation processes from molten (fluoride) salt medium
- Molten (fluoride) salt/liquid metal reductive extraction
- Gas extraction from the molten salt medium

2.1. Fused salt volatilization technique

The separation techniques known as ‘volatilization’ or ‘fluoride volatility’ are typical ‘dry’ processes that involve the fluorination of spent fuel with fluorine gas and subsequent separation of

resultant volatile compounds, represented mainly by uranium hexafluoride, from non-volatile fluorides, in the first instance from PuF_4 . There are two main volatilization techniques – a reaction between the fluorine gas and a fused salt and a reaction between the fluorine gas and a solid (powdered) material [7,8,4].

The volatilization technique based on bubbling of fluorine gas into fused fluoride salt containing elements forming volatile fluorides was studied in ORNL mainly during the MSRE program in 1960s and 1970s. The main objective of the program was the development and verification of a possibility to remove uranium (in the form of volatile UF_6) from the molten fluoride salt carrier (based on LiF – BeF_2 or LiF – BeF_2 – ZrF_4 mixtures). The processes were quite successfully verified with complete separation of uranium from the salt in 1968 [4]. Carrier molten fluoride salt, in which was uranium dissolved, was LiF – BeF_2 eutectic. Uranium was recovered from the carrier salt as uranium hexafluoride by sparging the salt with fluorine gas. Special equipment for continual fluorination of the salt was designed and realized [9]. The crucial part of the equipment was the continuous fluorination reactor with frozen wall for corrosion protection. The carrier molten salt containing dissolved UF_4 flowed into the top of the fluorination reactor and was contacted by a countercurrent stream of fluorine gas, which stripped out the uranium in the form of volatile UF_6 according to the following reaction:

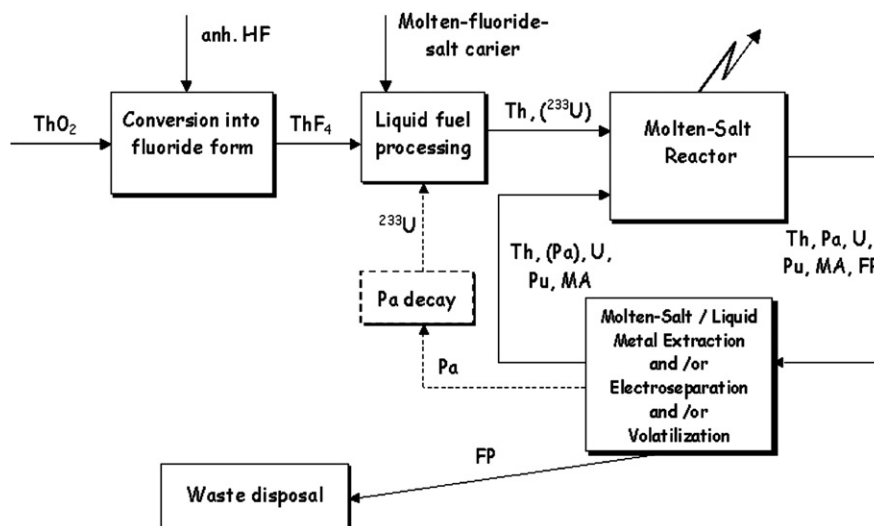
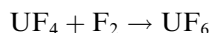


Fig. 1. Fuel cycle of Molten Salt Reactor working under ^{232}Th – ^{233}U cycle. MA – minor actinides, FP – fission products.

The working temperatures were in the range of 500–550 °C; the reactor walls coolant was NaK. The off-gas containing uranium hexafluoride, fluorine gas and volatile fluorides of some fission products (here mainly CrF_4 and CrF_5) passed through sorption column with NaF pellets heated to 400 °C for removal of chromium fluorides. UF_6 was then trapped at the same sorbent at 100 °C. Similar technology was under development in ORNL during ensuing MSBR program in the beginning of 1970s aimed mainly to design an on-line reprocessing scheme for Molten Salt Reactors working under ^{232}Th – ^{233}U fuel cycle [10].

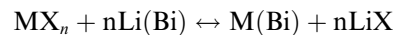
The technology of uranium removal by fused salt volatilization is still now widely discussed method as one of possible techniques within the on-line fuel reprocessing of future MSRs with Th-fuel. The removal of uranium from the fuel salt of MSRs is here a part of the protactinium removal process. Protactinium Pa-233 results in the reactor core from thorium Th-232 by nuclear reactions. The half-life of radioactive decay of ^{233}Pa is 27 days and its only daughter product is ^{233}U . However, the arising protactinium, which is also a mighty neutron poison, has to be immediately removed from the fuel salt circulating in the reactor to pre-empt undesirable nuclear reaction. Suitable technology for protactinium removal from the fluoride molten salt carrier is ‘molten salt/liquid metal reductive extraction process’ occasionally called also as a ‘metal transfer process’. Because of the fuel salt of MSR contains several percent of uranium in the form of uranium tetrafluoride UF_4 , it is proved, that a primary ura-

nium removal by fluoride volatilization of fused salt can save the amount of reducing agent ^7Li used for subsequent protactinium isolation. The simplified scheme of protactinium isolation process according to the ORNL proposal [4] is shown in Fig. 2.

2.2. Molten salt/liquid metal extraction and electrochemical separation technologies

During the MSRE and MSBR programs, which were in motion in ORNL in 1960s and 1970s, the main process proposed for fluoride fuel salt clean-up was a ‘metal transfer process’, which is rather known as ‘Molten salt/liquid metal reductive extraction’. The main purpose of the technology, within the MSR on-line reprocessing, is removal of fission products represented mainly by rare earth elements (lanthanides) from the circulating fuel salt [4,10].

Extraction to the liquid bismuth was proposed due to its suitable properties. Bismuth has a low melting point (271 °C), negligible vapor pressure in the temperature of interest (500–700 °C) and good solubilities of lithium, thorium, protactinium, uranium and lanthanides. Bismuth is also essentially immiscible with molten halides. Reductive extraction between metal in molten salt and liquid metal phases can be expressed by following general reaction:



in which a metal halide MX_n in the salt reacts with lithium from the bismuth phase to produce M in the bismuth phase and the respective lithium halide in

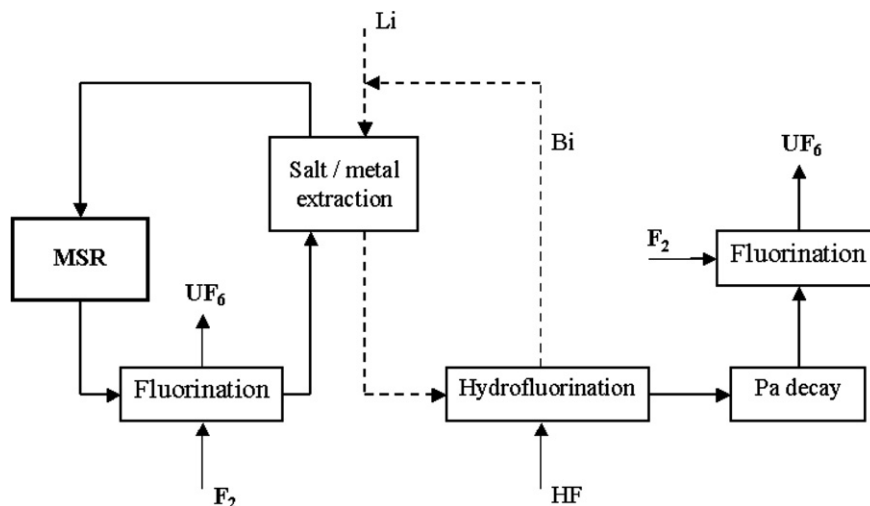


Fig. 2. Simplified scheme of protactinium isolation from MSR fuel.

the salt phase. There are three possible ways, how to influence selectivity of the method:

- technique utilizing dependency of distribution coefficients on used carrier molten salt and on concentration of reducing agent added in the form of alloy with molten metal (Bi);
- technique utilizing selective reducing agents (This technique can be hardly used in MSR fuel reprocessing due to strict requirement on the chemical composition of carrier molten salt.);
- non-selective technique using direct addition of high concentration of reducing agent into the liquid metal.

The distribution data obtained for elements included in MSR spent fuel between bismuth and carrier fuel salt ($\text{LiF}-\text{BeF}_2$) showed, that a multi-stage extraction process for step by step separation of lanthanides from thorium is impossible, because the separation factors are close to unity. Therefore, another separation system, between molten LiCl and liquid bismuth was chosen for separation of individual elements, but the common non selective extraction of all metals dissolved in carrier fluoride salt remained to be as the first stage [4,10].

Present knowledge and a significant progress in the development of electrochemical separation methods of actinides and lanthanides also from

molten fluoride salt media permits considerations, that electrochemical processes should assert themselves within the spent fuel on-line reprocessing of future Molten Salt Reactors. The development of suitable technologies is in significant progress in several research laboratories in Europe (mainly in France), Japan, Korea, USA and Russia and first flow-sheets of MSR spent fuel reprocessing were brought out. A conceptual flow-sheet of MSR on-line spent fuel reprocessing, associating the Molten salt/liquid metal reductive extraction technology and the electroseparation process in molten fluoride salt medium was proposed by research institution in the Czech Republic in the frame of national MSR technology development [11]. The flow-sheet is shown in Fig. 3. The concept is based on primary non-selective Molten salt/liquid metal reductive extraction and subsequent selective electrochemical separation method. Li and molten Bi or Cd is planed to be used as reduction and extraction agents, respectively.

The reason of such a combination of salt/metal extraction and electroseparation resides in fact that the lanthanides should be removed prior to the actinides, which should remain in the main fuel stream and go back to the Molten Salt Reactor. According to the experimentally measured thermodynamic properties of selected lanthanides and actinides, fluorides of the lanthanides are more stable and cannot

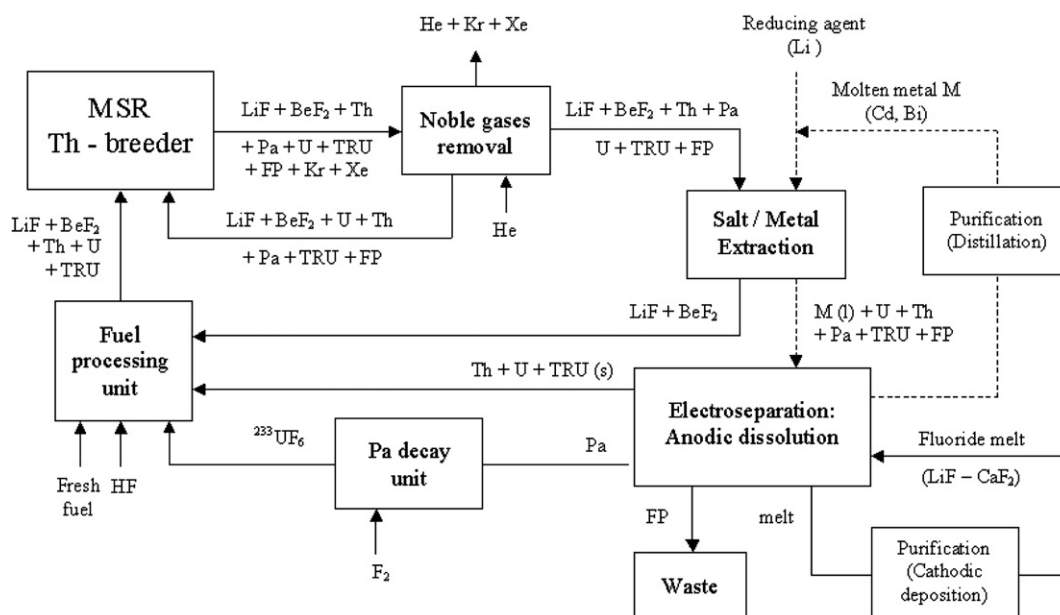


Fig. 3. Conceptual flow-sheet of MSR on-line reprocessing technology based mainly on Molten salt/Liquid metal reductive extraction and Electroseparation processes. TRU – transuranium elements, FP – fission products (lanthanides).

be reduced neither electrochemically nor chemically prior to actinides without simultaneous reduction of the latter. The proposed flow-sheet is based on the removal of all elements from the carrier salt in a form of metallic mixture, from which it would be possible to selectively remove only lanthanides by the Electrochemical Anodic Dissolution method. The fluoride molten salt with satisfactory thermochemical stability has to be applied, the carrier melt composed, e.g., of LiF-CaF_2 eutectic mixture has been proposed, because of the thermochemical stability of BeF_2 , which is of else the component of carrier fuel salt, is unsatisfactory for this purpose [12,13].

Anodic Dissolution method is based on selective electrochemical oxidation of separated elements in reduced form. The differences in their deposition red-ox potentials provide the selectivity, while the more positive potential is applied, the less stable compounds can be formed and respective metal can be dissolved. It was experimentally proven that fluorides of the lanthanides are more stable than fluorides of the actinides, thus they can exist at more negative potentials. If the step-by-step increasing potential is applied, the lanthanides are dissolved as the first at more negative potentials and the actinides remains in the metallic form.

The instrumentation of the method is provided by two or three electrodes immersed in the carrier fluoride melt and connected to tuneable stabilized voltage source or potentiostat. Used electrodes are working liquid electrode with controlled potential, counter (auxiliary) electrode providing the charge transfer and possibly reference electrode in electrochemically more complicated systems. The separated metallic mixture can be directly connected as working electrode or can be inserted into the special conductive electrode basket. After the process starts, the dissolved elements are electrotransported to the counter electrode and reduced there back to the metallic form [14].

The electrochemical method dealing with the Cathodic Deposition can be used for removal of dissolved ions, which are less stable than used carrier melt. The process resides in gradually decreasing potential of working electrode and reducing of presented ions, while the lesser the potential is, the more stable compounds are reduced. The instrumentation is similar to the above-mentioned case,

however both the working and counter electrodes could be solid.

The proposed technology of the on-line reprocessing of MSR fuel should be further replenished, according to the ORNL proposal, by the gas extraction technique using a helium bubbling system for removal of neutron poisoning gases, xenon and krypton, issuing by nuclear reaction and by the uranium isolation from decaying protactinium.

3. Conclusion

As the future deployment of Molten Salt Reactors seems to be realistic, the relevant molten salt technologies of their fuel cycle have to be developed in due time. The assignment will be very exacting and probably hardly feasible by an individual country. Therefore the joint international co-operation will be necessary. Current R&D effort is provided only in a few countries mainly in the Czech Republic, France and Russia, however the achieved results and the common pursuit to joint the effort in the international projects offer the realistic preconditions that the task will be solved successfully.

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