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Molten salts and nuclear energy production

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Abstract

Molten salts (fluorides or chlorides) were considered near the beginning of research into nuclear energy production. This was initially due to their advantageous physical and chemical properties: good heat transfer capacity, radiation insensitivity, high boiling point, wide range solubility for actinides. In addition it was realised that molten salts could be used in numerous situations: high temperature heat transfer, core coolants with solid fuels, liquid fuel in a molten salt reactor, solvents for spent nuclear solid fuel in the case of pyro-reprocessing and coolant and tritium production in the case of fusion. Molten salt reactors, one of the six innovative concepts chosen by the Generation IV international forum, are particularly interesting for use as either waste incinerators or thorium cycle systems. As the neutron balance in the thorium cycle is very tight, the possibility to perform online extraction of some fission product poisons from the salt is very attractive. In this article the most important questions that must be addressed to demonstrate the feasibility of molten salt reactor will be reviewed.

1. Introduction

The main characteristic of nuclear energy production is the large energy release by one nuclear reaction (fission) compared to any chemical energy production reaction (at least a factor 10^7). Therefore, the choice of a coolant able to transfer, under irradiation, large amounts of heat is an important concern. This choice is further reduced when the nuclear properties of the constituents of the possible fluids are taken into account. The objective of this paper is to discuss the possibilities offered by molten salts in nuclear energy production. First we discuss why molten salts based on fluorides or chlorides are an attractive choice. We will then discuss the elementary composition of the salt taking into account the nuclear properties (neutron capture and diffusion), the desirable chemical and physical properties and how the necessary chemical treatment depends on the particular use envisaged. Molten salts are particularly interesting because they may be used either for the whole heat transfer between two places or as both heat and fuel carriers in reactors. Early development of molten salt reactors using the thorium cycle will also be briefly discussed in the paper.

2. Why molten salts in nuclear energy production?

A nuclear reactor core is a place where a large amount of heat is produced in a very limited

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volume. This heat has to be transported out quickly in an environment characterized by high neutrons fluxes and high radiation levels. There are very few possible fluids able to effectively bear these constraints and allow rapid transfer of heat to the first heat exchanger. The main properties of the coolants which are in use in the nuclear reactors are given in Table 1.

Molten salts exhibit the most appealing properties which explain why they were taken in consideration very early in the nuclear energy production community:

- Unlike gases, they have the largest heat capacity per unit volume without any need of pressurisation [3], and a reasonable density.
- Their high boiling point and low vapour pressure allow very high temperatures which are needed for high efficiency conversion cycles to produce electricity or hydrogen.
- Their transparency allows in-site inspection.
- They have great insensitivity to radiation which prevents gas creation and changes in chemical properties.

Another interesting feature is that each fluorinated actinide is more or less soluble in a molten fluoride salt and may be mixed with chosen salts according to the requested properties. This idea leads to the molten salt reactor where the fuel is part of the salt moving in and out of the core. Two experiments with molten salt reactors were successfully conducted in Oak Ridge: the Aircraft Reactor Experiment (ARE) was running for approximately 100 h around 1955 at a thermal power of 2.5 MWth. Ten years later the molten salt reactor experiment (MSRE) started [7]. It was an 8 MWth reactor initially fuelled with ^{235}U and finally with ^{233}U which ran for four years without problems. As the power was low, there was no need to perform one-line salt reprocessing. This preparatory work led the ORNL team to present a power reactor project, the Molten Salt Breeder Reactor [1] fuelled with thorium and ^{233}U as fissile material. As maximising the breeding ratio was the main objective, a very constrained salt reprocessing was required where the entire salt volume (48 m^3) had to be reprocessed in 10 days with efficiencies depending on the element (e.g. 100% for Pa). Besides the demonstration of the validity of the concept, the experiments have given very important informations about the corrosion of structural materials and graphite and led to the choice of Hastelloy-N for the tank and the pipes. In the molten salt reactor, the question of the fuel conditioning, of its cladding and of the resistance to high temperature, irradiation and corrosion of the solid fuel elements are avoided. The salt composition was designed to be continuously controlled and adjusted, thus there was no need of reactivity reserves inside the reactor and very high burn-up was possible.

Table 1
Main properties of the coolants used in the nuclear reactors

Coolant	Pressure (bar)	Volumic heat capacity ($MJ/m^3/K$)	Boiling temperature (°C)
He	60	0.02	
CO_2	60	0.05	
H_2O	250	4.07	Supercritical
Na	1	1.12	883
LiF–BeF_2–ThF_4	1	4.54	>1430

3. How to choose the salt?

Several competing constraints have to be taken into account.

3.1. Nuclear constraints

Since the salt spends a lot of time in a very large neutron flux, the neutron capture probability by the salt constituents is very important. A large capture cross-section leads to a loss of neutrons which may not be acceptable for the reactor operation, so elements with the smallest cross-sections are preferred. For example, natural lithium (where ^6Li has a large capture cross-section) has to be isotopically separated. Only ^7Li is acceptable in the core. The second consequence of the capture is the production of a new isotope which may be undesirable for reasons of radioprotection, unacceptably large neutron cross-section, or chemistry. For example, production of long lived isotope such as ^{36}Cl from capture on ^{35}Cl is undesirable. The diffusion properties of the neutrons on the components and the atomic number of the components also have an influence on the neutron spectrum in the reactor core (neutrons become more or less quickly thermalized depending on the salt composition).

3.2. Chemical constraints

Following the choice of a good coolant with acceptable viscosity and good nuclear properties, the main requirement for the salt is its stability to avoid circulation problems due to solid precipitation. Precipitation of solids may occur due to cooling and a good knowledge of the phase-diagram is required. However, precipitation may also occur over time from the build-up of fission products and actinides produced by the nuclear reactions, or accidental contamination (by water vapour for instance), so a continuous control has to be made.

On-line redox potential control is also needed to avoid corrosion of the pipes by the salt and by some fission products. Te, C and Ni-based steels are known to withstand corrosion to an acceptable level. For other materials, protective liners may be needed and studied.

Finally, further off-line reprocessing must also be considered. Assuming that bubbling with an inert gas is able to quickly remove gaseous elements (Xe, Kr, Te, ...) and some insoluble metallic elements (Mo, ...), a further reprocessing step is still required to remove lanthanides (neutron poisons) from the salt. Up to now, no chemical processing procedure has been validated to remove lanthanides in presence of thorium fluoride and it may be necessary to remove thorium after Uranium. Uranium may be removed first by gaseous fluorination producing UF_6. The salt choice may interfere with the reduction methods (with production of an alloy) that are anticipated to remove various components (U, Pu, Th, minor actinides) prior to lanthanides extraction and this has to be taken into account.

4. Possible applications

The multiple applications which are now foreseen for the molten salts in the nuclear energy production domain are the following:

1. *Salt loops for high temperature heat transfer:* For example, future nuclear plants designed for hydrogen production are assumed to be based on electrolysis or on various thermochemical processes, which anyway require the highest temperatures. Some very high temperature reactors under development are designed with gas coolants which are not well suited to long distance heat transfer between the reactor and the hydrogen production plant which must be separated for safety reasons. The liquid salts due to their good thermodynamic properties are good candidates for that heat transfer.

2. *Liquid coolant in solid fuel reactors:* Molten salts are some of the very few fluid coolants which are able to sustain temperatures needed for the proposed direct hydrogen production methods ($T > 850$ °C). Hence, in the United States, one of the VHTR concepts studied is the advanced high temperature reactor (AHTR) [2], a thermal neutron reactor with conventional fuel (^{235}U and Pu) cooled by molten fluorides. Molten salt may also be used as a coolant in a solid fuel fast reactor (LSFR) to replace liquid metals or gas without limitations on temperature or pressure. In the fusion case, it may play a role both as heat carrier and tritium source due in that case to neutron reaction on ^{6}Li.

3. *Liquid fuel reactors:* The concept, which was studied with the MSRE at ORNL, has many interesting features which allowed study of its use for many different applications. The first was the MSBR project, to produce energy via the thermal thorium cycle, which will be discussed later. Thermal or fast neutron molten salt reactors with uranium–plutonium or thorium–uranium cycle are now considered in several institutions. They may allow safety questions to be overcome and high temperature and pressure problems for energy production in breeder reactors to be solved. Furthermore, they are also considered for critical or sub-critical transmutation systems as fuel fabrication difficulties are avoided.

4. *Reprocessing of spent fuels by pyro-reprocessing methods:* Up to now the only industrial process at work to reprocess the spent nuclear fuel is the hydrometallurgical liquid–liquid extraction process which is sensitive to a high level of radiations. With the new fuel supports (nitride, carbide, metal) foreseen and the high radiation level which will characterize the innovative concepts, the limits of this process may be reached quickly. As fuel reprocessing is more or less unavoidable for future nuclear energy systems, pyro-reprocessing where the salts are much less sensitive to radiations may be the only other solution and thus is currently studied in many laboratories.

5. Thorium cycle and molten salts reactors

Nuclear production has up to now been only based on the use of ^{235}U. It is the only fissile element available in nature. Moreover, Fig. 1 shows that there are only two other possibilities for nuclear

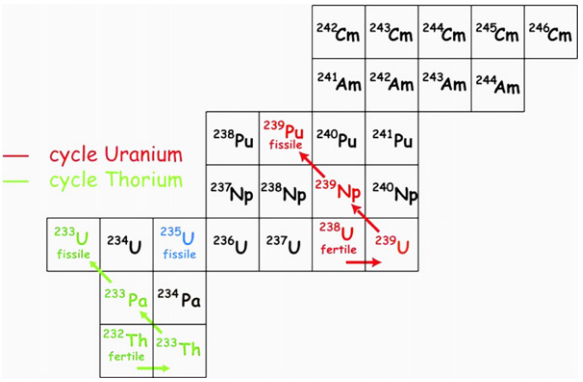

Fig. 1. Actinide chart.

energy production, namely the fertile nuclei ^{238}U and ^{232}Th. After a neutron capture and two β-decays, the fissile nuclei ^{239}Pu and ^{233}U are produced and may be used as fuel in reactors. The only way the neutron capture can occur at a sufficient rate is to place the fertile element in a reactor with enough fissile material to start the chain reaction. The reactor will be a 'breeder' if it is able to produce a number of fissile nuclei equal or greater than the number of fissile nuclei that disappear by capture or fission. If ν is the number of neutrons emitted by fission and α the ratio of capture cross-section divided by the fission cross-section induced by neutrons as a function of energy, the available neutrons left by the breeding is given by $N_b = \nu - 2(1+\alpha)$. This quantity is plotted in Fig. 2 for the two fertile elements. It appears that, as the available neutron number is slightly larger than 0, breeding is possible for the whole neutron energy spectrum for thorium whereas it is only possible for neutron energy larger than a few 10 keV for plutonium. This explains why, if plutonium is produced and partly burnt in the light water reactors, it is impossible to reach desirable breeding ratio with a thermal neutron spectrum in the U/Pu cycle. The main advantage of the thermal spectra is that the required fissile material for starting the chain reaction is smaller (factor up to six) than for the fast neutron reactor, so the deployment is easier.

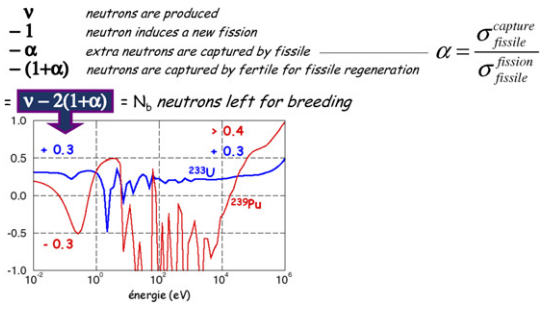

Fig. 2. Available neutrons.

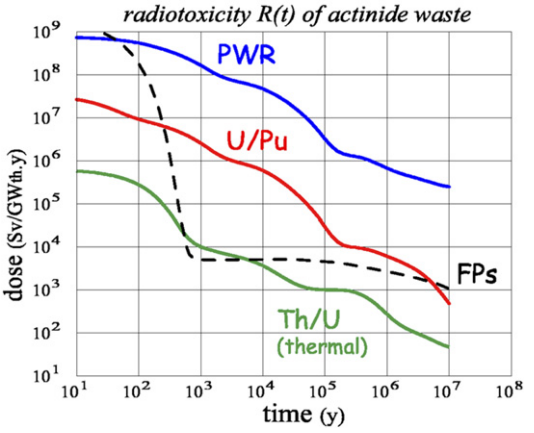

Fig. 3. Radiotoxicity of the actinides wastes.

Another desirable feature of the thorium cycle is the lower production of actinides which are the main contributors to the radiotoxicity of the spent fuel. Fig. 1 shows that five successive neutron captures are necessary to reach the neptunium which is the lighter minor actinide, whereas the plutonium is already right in the middle of the actinides. The radiotoxicity which tries to assess the risk due to the spent fuel of the various fuel cycles plotted as a function of time is given in Fig. 3 which shows clearly the advantage of the thorium cycle. To give an idea of the level of the curves presented in that picture, the dose associated with the natural uranium which would be needed to produce one GWe · Year is 5×10^5 Sv. The radiotoxicity of the spent fuel coming from a PWR and stored without reprocessing is given by the upper blue curve; it reaches the original and natural radiotoxicity of uranium only after 10^7 years.[1] With the U/Pu cycle in fast neutron reactors, the produced radiotoxicity is reduced by an order of magnitude (middle red curve). Another order of magnitude is still obtained with the thermal thorium cycle operating in molten salt reactors (lower green curve). The radiotoxicity produced by the fission products is the same whatever the cycle and is given by the dashed curve. As the number of available neutrons is as small as 0.3 in the thorium cycle, it is very important to mini-

[1] For interpretation of color in Fig. 3, the reader is referred to the web version of this article.

mise all the potential neutron losses. As some fission products are very neutron capturing, it is very desirable to remove them as soon as possible from the reactor core and it is one of the reasons why the thorium cycle has been linked to the molten salt reactors from the start.

6. Molten salt reactors today

Starting from the MSBR project, many studies have been made in several countries concerning the possible uses of the MSR. There was an important renewal of interest when the transmutation of long life nuclear wastes became a big concern. Studies concerning critical and sub-critical reactors loaded in some cases directly with spent fuel fluorides were also performed. A review concerning the various aspects of the MSR has been made during the EURATOM Concerted Action MOST [6]. Future studies have been separated into five groups which are: design and safety, reactor physics, fuel salt chemistry, material-mechanics, fuel salt clean-up. Several concepts are under evaluation but a special emphasis is put on the simplest design, the thorium molten salt reactor (TMSR). In this concept [4], the reactor is fuelled only with Th and ^{233}U, the required breeding ratio is close to one and the reprocessing has been simplified as much as possible. Only bubbling to extract gaseous products and some noble metals and salt property control are made on line. The remaining part of the reprocessing is being performed in a separated unit where the whole core volume is processed in at least six months. Some designs have been found to obtain good reactivity coefficients [5]. The goal of the works undertaken in the aforementioned five domains is to demonstrate as soon as possible the feasibility of molten salt reactors. Molten salt reactors are also studied as waste incinerators because they allow avoidance of the difficult problems connected to the fabrication of the solid fuel.

7. Summary

Nuclear energy remains a good possible technology to produce large amounts of energy in favourable conditions of safety and durability without large greenhouse gas emissions. Several concepts are now under study in order not only to produce electricity with high conversion efficiency but also to supply high temperature heat for combined cycle, hydrogen production and water desalinisation. In the case of large increase in nuclear energy production, the question of the fissile material resources and of the produced amount of wastes will become an important concern. The opportunities offered by molten salts in general and in particular for the thorium cycle may lead to increased interest in these systems. A main concern will be the compatibility of the salt with the various materials in close contact with it at high temperatures and high irradiation levels. Further studies will need to be carried out on these aspects along with the development of the salt control and reprocessing.

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