


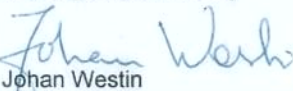
# CONQUER CORROSION

## Key issues of the lead-cooled fast reactor design

Mathias Hareland, MSc Thesis  
Uppsala University



## Conquer corrosion

<b>From</b> Vattenfall Research and Development AB	<b>Date</b> 2011-03-15	<b>Serial No.</b> U 10:124
<b>Author/s</b> Mathias Hareland, MSc Thesis, Uppsala University	<b>Security class</b> Open [S1]	<b>Project No.</b> PR.244.7
<b>Customer</b> Eva Halldén Vattenfall AB BU Nuclear Power SE-162 87 Stockholm	<b>Reviewed by</b>  Anna-Maria Wijberg	
	<b>Issuing authorized by</b>  Johan Westin	
<b>Key Word</b> Nuclear power, Generation-IV, lead cooled fast reactor, LFR, corrosion, MAXTHAL, MYRRHA, Lead-bismuth eutectic, LBE	<b>No. of pages</b> 39	<b>Appending pages</b> 6

### Summary

The lead-cooled fast reactor (LFR) is one of the concepts of the Generation IV reactor systems. There are some issues that have to be solved before a research or commercial LFR can be built. The objective of this thesis was to identify these key issues and analyse them by studying results from previous research: choice of fuel, corrosion on structural materials and corrosion/erosion on pumps.

The major fuel candidates for the LFR are MOX fuel (Mixed OXide fuel), metallic fuel, nitride fuel and carbide fuel. Nitride fuel has desirable properties but its production is more difficult than for MOX fuel.

Most of today's commercial steels are not corrosion resistant at higher temperatures but they could possibly be used for an LFR test demonstrator with an operating temperature lower than 450 °C. A new type of steel called oxide dispersion strengthened (ODS) steel and a new ceramic material MAXTHAL both show promising corrosion resistance even at higher temperatures.

By controlling the oxygen concentration a protective oxide film is produced. Flowing liquid coolant causes erosion and wears down the oxide film. Pumps are exposed to coolant velocities of 10-15 m/s causing both erosion and corrosion. There is no solution today, but MAXTHAL shows promising results in tests with liquid lead of low velocity. There are also other issues unsolved, such as irradiation damage on structural materials, thus more research is needed.

Economic and political aspects were not covered in this study. This thesis work was performed at Vattenfall Research and Development AB.



## Distribution list

Company	Department	Name	Number of
Vattenfall	PN-T	Eva Halldén	1 + pdf
Vattenfall	PN-T	Jan-Erik Lindbäck	1 + pdf
Vattenfall	AR-G	Ali Etemad	1 + pdf
Vattenfall R&D	AE-DN	Patrik Andersson	pdf
Vattenfall R&D	AE-DNM	Johan Westin	pdf
Vattenfall R&D	AE-DNM	Hans Henriksson	3 + pdf
Vattenfall R&D	AE-DNM	Anna-Maria Wiberg	3 + pdf
Vattenfall R&D	AE-DNM	Karin Andgren	pdf
Vattenfall R&D	AE-DNM	Margaretha Engström	pdf
Vattenfall	PN-T	Daniel Westlén	pdf
Vattenfall	PN-T	Pär Lansåker	pdf
Vattenfall	PN-H	Jan Blomgren	pdf
VE Nuclear Energy	PN-ETK	Andreas Hüttmann	pdf
Vattenfall Nuclear Fuel	PN-NR	Andreas Lidén	pdf
Ringhals	VA-NRRTF	Pål Efsing	pdf



# Table of Contents

Page

<b>1</b>	<b>INTRODUCTION</b>	<b>1</b>
1.1	Goals	1
<b>2</b>	<b>METHOD</b>	<b>1</b>
2.1	Identification of key issues	1
2.2	Gathering of information	2
2.3	Restrictions	2
2.4	Report outline	2
2.4.1	Chapter 3, LFR a Generation IV reactor concept	3
2.4.2	Chapter 4, Fuels	3
2.4.3	Chapter 5, Corrosion in structural materials	3
2.4.4	Chapter 6, Erosion in pumps	3
<b>3</b>	<b>LFR A GENERATION IV REACTOR CONCEPT</b>	<b>3</b>
3.1	Fast reactors	4
3.2	LFR design	4
3.3	Comparison of the coolants lead and LBE	5
3.3.1	Polonium	6
3.4	The MYRRHA project	7
3.4.1	Design parameters	7
<b>4</b>	<b>FUELS</b>	<b>9</b>
4.1	MOX fuel	10
4.2	Metallic fuel	10
4.3	Nitride fuel	10
4.3.1	Compatibility with cladding and coolant	12
4.4	Carbide fuels	13
4.5	Comparison of the fuels	13
<b>5</b>	<b>CORROSION IN STRUCTURAL MATERIALS</b>	<b>14</b>
5.1	The corrosion phenomenon	15
5.1.1	Solubility of iron, chromium and nickel in lead and LBE	17
5.2	Oxygen concentration in molten coolant	20
5.2.1	Oxygen control	21
5.2.2	Oxygen concentration monitoring	22
5.3	Embrittlement and mechanical properties	23

5.4	Commercial structural materials available today	24
5.4.1	316-L steel	25
5.4.2	SS316 steel	25
5.4.3	HT-9 steel	25
5.4.4	T-91 steel	26
5.4.5	EP-823 steel	26
5.4.6	20Kh13 steel	27
5.4.7	Summary of commercial steels	27
5.5	Future steels	28
5.5.1	Corrosion tests of ODS steels with different compositions	28
5.5.2	Test with $C_{O_2} = 10^{-8}$ wt.% at 550 °C	29
5.5.3	Corrosion tests of ODS steels with different compositions	29
5.5.4	Test with $C_{O_2} = 10^{-8}$ wt.% at 550 °C	29
5.5.5	Test with $C_{O_2} = 10^{-6}$ wt.% at 650 °C	29
5.5.6	Summary of the tests	30
5.6	New ceramic materials	30
<b>6</b>	<b>EROSION IN PUMPS</b>	<b>32</b>
<b>7</b>	<b>DISCUSSION</b>	<b>32</b>
7.1	Reactor coolants	32
7.2	Fuels	33
7.3	Corrosion	33
7.4	Pumps	34
7.5	Further work	34
<b>8</b>	<b>CONCLUSIONS</b>	<b>35</b>
<b>9</b>	<b>ACKNOWLEDGEMENT</b>	<b>35</b>
<b>10</b>	<b>REFERENCES</b>	<b>36</b>



# Appendices

Number of Pages

<b>APPENDIX 1</b>	MYRRHA vessel configuration	4
<b>APPENDIX 2</b>	Chemical formulas for oxide layers	1
<b>APPENDIX 3</b>	Formulas for carbide fuels	1



# 1 Introduction

There are several different fast reactor designs in the world of which the lead-cooled fast reactor (LFR) is one. Fast reactors have been of interest ever since the beginning of the atomic age due to their potential to enhance resource utilization and improve waste management. Research and development of lead-cooled fast reactors have been performed for several decades, for example Russian submarines have used lead-cooled fast reactors for about 40 years. The reason why there are no conventional or research LFRs in use today is because of several technical difficulties. One of them is the material issue; molten lead is very corrosive against structural materials at the high temperatures used in LFRs (1). These issues have to be solved before a research or commercial reactor can be built. A research reactor is planned in Belgium, which hopefully will provide more data and knowledge about this reactor concept.

The lead-cooled fast reactor is one of the concepts comprising the Generation IV reactor systems. High goals have been set on these systems in terms of sustainability, safety and reliability, economics and proliferation resistance and physical protection (2). It is difficult to say when the first LFR meeting the criteria of Generation IV will be built. From a Vattenfall perspective it is important to have a general understanding of the LFR and to understand what issues remain to be solved before these reactors can be built.

## 1.1 Goals

The goal of this project was to identify and analyze the main difficulties of the lead-cooled fast reactor concept and explain what issues remain to be solved before a commercial reactor can be built.

# 2 Method

The study was mainly based on a literature study and some interviews, which intended to explain the key issues with LFRs.

From the beginning, several issues were considered, but after a selection process the key issues could be identified.

## 2.1 Identification of key issues

This study investigated several scientific articles in order to identify the key issues. Several of them pointed out corrosion on structural materials as being of great importance. Fuel issues were mentioned only rarely, though several different kinds of fuels were brought up. An expert in the area, Janne Wallenius from KTH, was asked if

corrosion and fuels are the key issues for LFR design. His opinion was that corrosion on structural materials is indeed a key issue. He also pointed out erosion and corrosion on the pumps in LFRs. Fuel was not mentioned as one of the key issues, but it was decided to investigate them as well in order to see if one of them is more optimal for usage than the others. In Sodium-cooled Fast Reactors (SFRs), which is another Generation IV concept, the fuel is exposed to a similar environment as in LFRs. Hence it came naturally to consider the fuels that have been investigated for SFRs.

From this selection process it was decided to focus the study on the choice of fuel, corrosion on structural materials and corrosion/erosion on pumps as they were regarded as the key issues.

## **2.2 Gathering of information**

Information for all topics was mainly obtained from reading scientific articles. The majority of these articles were obtained from databases linked to Uppsala University's online library and Google scholar. Some information however was obtained by mailing questions to experts in the area, for example people at KTH and people involved in the MYRRHA project. Another valuable source of information was study visits to research facilities like the fuel lab and TALL loop at KTH. TALL is a lead-bismuth eutectic (LBE) loop that simulates flow of liquid metal coolant. The fuel lab performs research on nuclear fuels, but mostly nitride fuel. Before using a scientific article its abstract and conclusions were read in order to see if the content was of any use. If the abstract and conclusions contained valuable information the article was saved for later use.

This work routine kept going on until enough information had been gathered in order to explain the key issues. Some additional scientific articles were gathered during the writing of the report in order to fill some gaps of information.

## **2.3 Restrictions**

This report focuses on the following technical aspects of the LFR; structural materials, pumps and fuels. Examples of issues left out, due to the selection process described in section 2.1, were strains on materials in the core, fuel encapsulation, environmental aspects and reactor design. No political or economic aspects were taken into consideration in this study.

## **2.4 Report outline**

Presented below is a short explanation of each chapter of this report.

#### **2.4.1 Chapter 3, LFR a Generation IV reactor concept**

This chapter includes an explanation of the LFR properties as well as a comparison of the two proposed coolants; lead and lead-bismuth eutectic. MYRRHA is mentioned because it is a large planned experimental research facility that is going to use LBE as coolant.

#### **2.4.2 Chapter 4, Fuels**

In this chapter four different fuels, mixed oxide (MOX), metallic, nitride and carbide fuels, are presented and compared.

#### **2.4.3 Chapter 5, Corrosion in structural materials**

This chapter contains results from corrosion tests on commercial steels available today and new steels. The results were compiled from scientific articles. Corrosion tests on a new ceramic material called MAXTHAL are also presented. Furthermore, this chapter includes a corrosion theory section as well as an explanation of oxygen control. An oxide layer on the structural material can give a protection against corrosion.

#### **2.4.4 Chapter 6, Erosion in pumps**

Issues with LFR pumps are presented here as well as potential solutions. The pumps are needed in a commercial size reactor in order to induce circulation in the coolant, which is needed for the cooling purposes.

### **3 LFR a Generation IV reactor concept**

No commercial or research LFR exists at the moment but a lot of research is going on in the world. Two planned research reactors are ELECTRA and MYRRHA. ELECTRA is a proposed project and its planned power is around 1% of MYRRHA's power. Due to the larger scale of the MYRRHA project it is mentioned more in section 3.4 (1), (11).

### 3.1 Fast reactors

Fast reactor designs have a high energy neutron spectrum as they do not moderate<sup>1</sup> neutrons. This allows a fast reactor to use breeding. The definition of breeding is when a reactor generates new fissile material at a higher rate than it consumes it (3).

In the breeding process,  $^{238}\text{U}$  is used to produce the fissile isotope  $^{239}\text{Pu}$ . Natural uranium consists of 99.27 %  $^{238}\text{U}$  and converting  $^{238}\text{U}$  to  $^{239}\text{Pu}$  is a way to enhance the resource utilization significantly (4). Spent nuclear fuel contains long-lived radioisotopes. In fast reactors, it is possible to transmute these actinides into isotopes with shorter half-lives. This would in turn reduce the burden on the nuclear waste disposal (5). Hence, fast reactors have the potential to both enhance resource utilization and reduce the lifetime of the nuclear waste.

### 3.2 LFR design

There are several different options when it comes to the size of lead-cooled fast reactors; one of them is a so-called battery reactor.

This type is planned to have a power of about 50-150 MWe and is supposed to run for 10-30 years without refueling due to breeding (2). The reactor is cooled by natural convection and there is therefore in no need of pumps. This reactor is intended to meet market demands on small electrical grids. Countries without an indigenous fuel cycle infrastructure and well developed electrical grids can therefore take benefit from this kind of reactor. The LFR concept also includes larger plants with power over 1 GWe (2). This larger reactor will have pumps to force circulation in the coolant. The fuel recycle time will be shorter for the larger plants, around eight years.

---

<sup>1</sup> Moderate: Slow down neutrons to a lower energy.

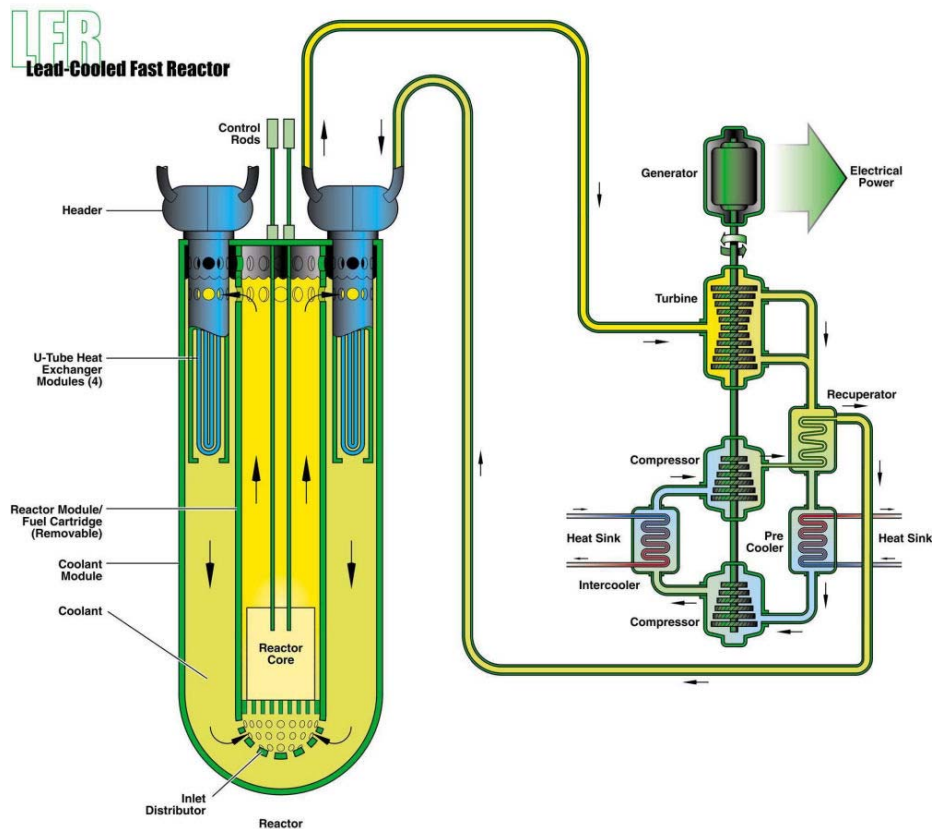


Figure 1: Lead-Cooled Fast Reactor design for the larger plant (2).

### 3.3 Comparison of the coolants lead and LBE

There are two possible choices of coolant for the LFR concept, one of them is pure lead and the other one is lead-bismuth eutectic (LBE). A eutectic is a mixture of different chemical compounds that has a lower melting point than all individual compounds (6).

Lead and LBE are similar in many ways. One difference is the melting point; for lead it is 328 °C and for LBE it is 125 °C (7). A lower melting temperature reduces the risk of coolant freezing which is an event that should be avoided. LBE is the best choice of coolant regarding this criterion. A typical design of a commercial reactor is planned to have an outlet temperature of 800 °C and therefore the freezing of lead will be of lesser concern (8). To avoid coolant freezing redundant electrical heaters are proposed to be used(7). There are some other properties of LBE that are not desired. One disadvantage is the higher cost in comparison to pure lead. Another problem with LBE is that polonium can be formed from irradiated bismuth at a factor 104 larger than in lead (7)

Basic physical properties of lead and LBE are shown in table 1.

**Table 1: Physical properties of lead and LBE at 427 °C. Both coolants have high boiling temperatures and densities. Their different melting points are also displayed (7).**

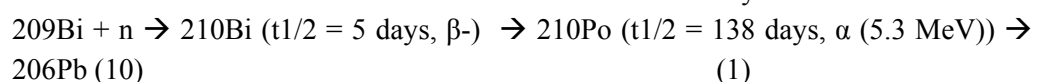
Coolant	Lead	LBE
$\rho$ [g/cm <sup>3</sup> ] (Density)	10.48	10.45
$T_m$ [°C] (Melting point)	328	125
$T_b$ [°C] (Boiling point)	1750	1670
$c_p$ [kJ/kg·K] (Specific heat)	0.15	0.15
$k$ [W/m·K] (Thermal conductivity)	16	13
$v_{max}$ [m/s] (Velocity)	2.5	2.5

Densities for both lead and LBE decrease with higher temperatures (9). With this physical property it is possible for both coolants to have a natural circulation due to the changes in their densities. Hot coolant floats up in the reactor tank and less hot coolant sinks down to the bottom, which can help to remove heat from the fuel (1).

A conclusion that can be made regarding the different coolants is that pure lead is more advantageous than LBE, due to the formation of hazardous polonium in irradiated LBE

### 3.3.1 Polonium

Polonium is hazardous and formation of this element should therefore be avoided. Polonium can be created from irradiated bismuth and the decay chain is as follows:

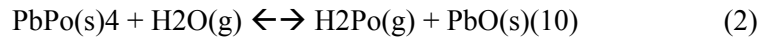


In LBE the polonium rapidly forms a compound with lead that is stable, only around 0.2 % of all created polonium stays in elementary form<sup>2</sup> (10). There is however a risk that this stable compound can form another hazardous compound. For example if the coolant comes in contact with water another compound is created, namely H<sub>2</sub>Po(g)<sup>3</sup> (Hydrogen polonide). Polonium water interaction can occur in case of a crack formation in a heat exchanger. Hydrogen polonide is created in the following way:

<sup>2</sup> Elementary form: The element has not formed any compounds with other elements.

<sup>3</sup> (g) stands for gaseous.





The best way to prevent this volatile gas from escaping out from the reactor pool is a continuous removal of polonium from the LBE coolant. Unfortunately, there exists no polonium extraction technology today that is suited for industrial scale (10).

### 3.4 The MYRRHA project

MYRRHA (Multi-purpose HYbrid Research Reactor for High-technology Applications) is planned to be a flexible lead-cooled fast reactor that can work in both a sub-critical<sup>5</sup> and critical<sup>6</sup> mode.

It is planned to be in full operation by 2020 and be used as an accelerator-driven system (ADS) for the first years (11). The purpose with an ADS is to burn transuranic elements (particularly Np, Am and Cm) more efficiently and safer than in critical reactors (11). An ADS consists of a proton accelerator that accelerate protons to higher energies. These high energetic protons collide with the coolant and generate neutrons to feed the sub-critical core. For each proton collision 15 neutrons are created on average (5).

The objective of the MYRRHA ADS is to demonstrate the technology required for the spallation neutron source, the accelerator driver and the coupling between the neutron source and the reactor core. After this phase, MYRRHA is planned to run as a critical reactor and focus on fuel and material research for the Generation IV reactors systems as well as produce radioisotopes for medical and industrial uses (11). MYRRHA will allow an evaluation of the demonstration and the performance of the transmutation concept on an experimental scale. This project will hopefully provide knowledge that can be used in the design of larger reactors in the future (12).

#### 3.4.1 Design parameters

In current design plans, MYRRHA is supposed to have a power of 57 MWth(11). It is supposed to use plutonium-uranium oxide (MOX<sup>7</sup>). It is the main option due to the better neutronic properties in fast neutron flux compared to the usual uranium dioxide. The MOX-fuel is planned to have 30 - 35 % Pu content (5).

---

<sup>4</sup> (s) stands for solidus.

<sup>5</sup> Sub-critical: More neutrons are used in the fission process than generated.

<sup>6</sup> Critical: Number of generated neutrons is the same as the number used.

<sup>7</sup> MOX (Mixed OXide) is a oxide fuel in which plutonium is mixed with depleted uranium.

A possible fuel cladding material is T91 Ferritic Martensitic Steel (see also section 5.4).

This is due to its resistance against swelling and creep<sup>8</sup> under large neutron flux. In the sub critical stage, a value of 0.95 has been considered as an appropriate level for  $k_{eff}$ <sup>9</sup>(13).

In tables 2 below, the parameters of MYRRHA are listed:

**Table 2: Physical dimensions and coolant properties for MYRRHA. The physical dimensions are in the first part and the coolant properties are in the second part (14).**

Dimensions	Values
Core external diameter	0.9 m
Core height	1.3 m
Fuelled length	0.5 m
Vessel diameter	4-5 m
Vessel total height	7 m
Vessel cover thickness	1-2 m
Gas plenum (if any)	0-0.5 m thickness
Primary coolant	LBE
Coolant pressure	Atmospheric and hydrostatic
Core inlet temperature	200 °C
Core outlet temperature (max)	350 °C
Coolant velocity in the core	2 m/s
Primary coolant flow rate	1400 kg/s
Secondary coolant	Water or possibly steam

<sup>8</sup> Creep: A slow deformation process.

<sup>9</sup> Ratio between the number of neutrons in one generation divided by the number of neutrons in the previous generation.

MYRRHA is planned to be used for several different applications as can be seen in the quote below.

“MYRRHA will serve as an irradiation tool for research in reactor and fuel cycle technology, reactor physics, material and fuel science, neutron physics and life sciences. Science at the proton accelerator will allow to make progress in different fields of fundamental physics.

MYRRHA will therefore form a cradle for the generation of new expertise in these science areas.” (5).

For more details about the core configuration of MYRRHA, see appendix 1.

## 4 Fuels

Development of fast reactor fuels from the 1960’s to the 1990’s has generated several types of fuels; such as carbide, metallic, nitride and MOX. It has been discovered that not all fuels are suited for the LFR concept.

Table 3 shows some physical properties of the four different fuels; MOX, metallic, nitride and carbide.

**Table 3: Physical properties of different fuels: MOX, metallic, nitride and carbide (15).**

Properties	MOX (U, Pu)O <sub>2</sub>	Metallic (U, Pu)Zr	Nitride (U, Pu)N	Carbide (U, Pu)C
Density [g/cm <sup>3</sup> ]	11.0	15.6	14.3	13.6
Density of fissile atoms [g/cm <sup>3</sup> ]	9.7	14	13.5	12.9
Thermal conductivity at 1000 °C [W/mK]	2.9	35	19.8	19.6
Melting point [°C]	2775	1160	2780	2480
Solidus temperature [°C]	2740		2720	2325

At a temperature slightly above the solidus temperature the material structure starts to change into a more liquid state. This process is continuous until the material reaches its melting point and becomes a liquid. The solidus temperature is often used as the fuel “melting” temperature in design and operation of reactors (16).

In a fast reactor the fuel rods operate at higher temperatures than in thermal reactors. Thus it is very important for the fuels to have high thermal conductivity in order to be able to efficiently conduct heat from the fuel centre.

Due to core neutronic requirements it is preferable for fast reactors to have a fuel with high density of fissile atoms because it provides with a better breeding performance (17), (18).

#### 4.1 MOX fuel

MOX fuel does not have a high thermal conductivity but it has a high solidus temperature. A high solidus temperature can to some extent compensate for a lower thermal conductivity because a high temperature is needed to change the material structure. MOX fuel has a lower density of fissile atoms than the other mentioned fuels (see Table 4) and is therefore less preferable for usage in a fast reactor in this aspect. Another property of MOX is that it does not react with liquid lead or LBE which is a strong advantage (19).

#### 4.2 Metallic fuel

A metallic fuel often consists of uranium, plutonium and zirconium. Published data indicates that these metals can dissolve in molten lead and LBE. If the fuel cladding stays intact there is no problem, but in case of fuel cladding failure the metallic fuel alloy may be dissolved by the coolant (20). This is the main reason why metallic fuels are not well suited as LFR fuel.

#### 4.3 Nitride fuel

Research on nitride fuel is performed in Sweden at KTH. Nitride fuels have both high density of fissile atoms and high thermal conductivity. They also have a high solidus temperature. Nitrides can confine chemically active elements and gaseous fission products to a higher degree than MOX. This is beneficial since some fission products act corrosively on cladding materials. This fuel is compatible with liquid lead and LBE in the sense that it does not dissolve in case of fuel-coolant interaction.

One disadvantage of nitride fuels, as well as carbide fuels, is that the fuel production is more complex in comparison to MOX fuels.

There are two main steps in the production of nitride fuels:

1. Synthesis of (U, Pu)N by carbothermic reduction of oxides.
2. Consolidation in the form of pellets by cold pressing and sintering.

This is the only method that is suitable for production of nitride fuel on a larger scale. In figure 2, the flow sheet for (U, Pu)N production is shown. The pellets are produced in the following chemical reaction:



Feed materials in this reaction are reduced uranium dioxide, plutonium dioxide, graphite and nitrogen. The carbothermic conversion part needs a high working temperature, the synthesis starts at 1150 °C under flowing nitrogen(21).

Unfortunately, there exists a problem with this production method in form of carbon and oxygen impurities that are inevitable. These impurities increase fuel swelling and the release of gaseous fission products. Another negative aspect regarding nitride fuel is the formation of radio-toxic  $^{14}\text{C}$  from  $^{14}\text{N}$  in the reactor(22). The reaction for the formation of  $^{14}\text{C}$  is as follows:



To deal with this problem  $^{15}\text{N}$  can be used instead of  $^{14}\text{N}$ . This is however much more expensive due to the enrichment of nitrogen that has to be done. By using enriched nitrogen, less  $^{14}\text{C}$  is produced and this conserves neutrons, which compensates for the higher cost (22). The neutrons are conserved because  $^{15}\text{N}$  does not capture neutrons to the same extent as  $^{14}\text{N}$  does. All unconsumed  $^{15}\text{N}$  in the fuel production is planned to be recycled and used again (15).

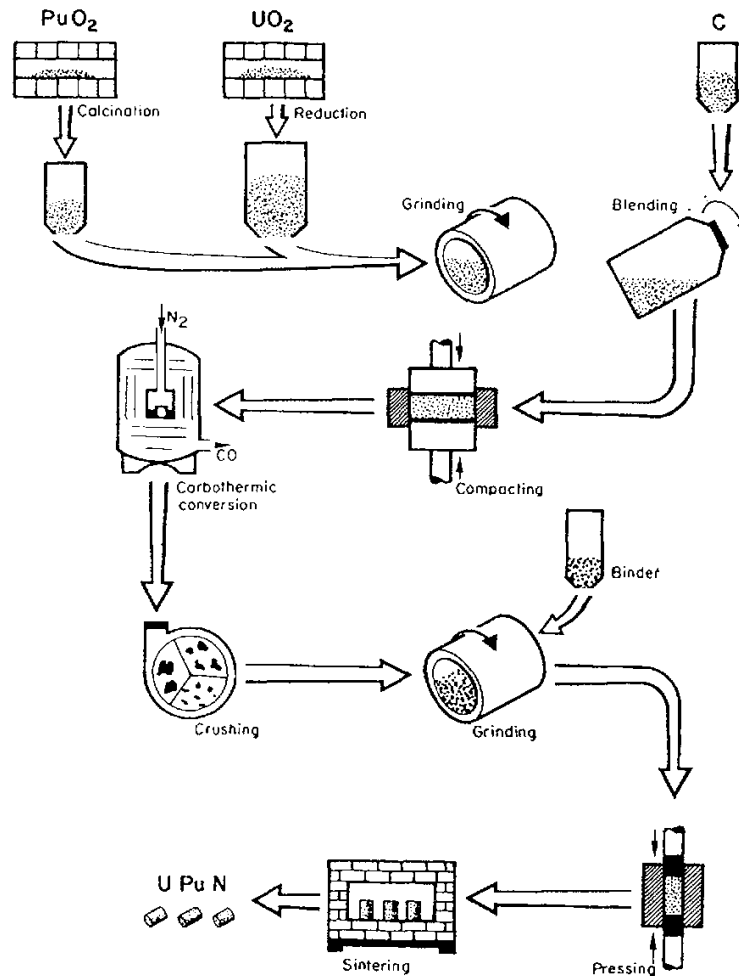


Figure 2: Flow sheet for (U, Pu)N(21).

#### 4.3.1 Compatibility with cladding and coolant

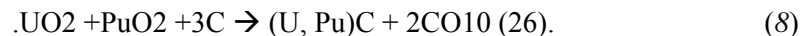
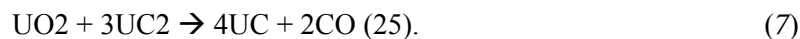
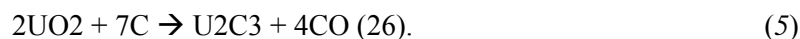
Some tests have been made on fuel interaction with coolant and cladding. These tests were carried out by Rogozkin et al. (24). A test at 650 – 800 °C for 2000 h was performed and the result was that no interaction between the fuel and the coolant or the fuel and the cladding had occurred. To test interactions in an emergency situation, tests at 1200 °C and 1300 °C for 5 h each were performed. No changes in the surface of the fuel or cladding material were detected(24).

#### 4.4 Carbide fuels

Like nitride fuel, carbide fuel have a high density of fissile atoms, a high thermal conductivity and are compatible with both liquid lead and LBE, in the sense that it does not dissolve in any of the coolants. The (U, Pu)C solidus temperature is lower than for nitride fuel and it has a thermal conductivity of about the same value.

There are several types of carbide fuels, such as UC, UC<sub>2</sub>, U<sub>2</sub>C<sub>3</sub> and (U, Pu)C. Uranium-monocarbide, UC, has a density of 13.6 g/cm<sup>3</sup> and a melting point of about 2390 ± 20 °C (25). This fuel type has metallic and ceramic properties, which means that it can conduct heat and tolerate high temperatures, and its thermal conductivity increases for temperatures over 400 °C (25). The densities of UC<sub>2</sub> and U<sub>2</sub>C<sub>3</sub> are 11.68 g/cm<sup>3</sup> and 12.88 g/cm<sup>3</sup> respectively(25). Data for (U, Pu)C are shown in Table 3 on page 16.

Here follows the chemical formulas for the different carbide fuels.



Similarly to nitride fuels, these fabrication processes are more difficult than for oxide fuels (17).

#### 4.5 Comparison of the fuels

As described above, metallic fuel is not well suited for a LFR, mainly because of its solubility in liquid lead and LBE. MOX has a lower density of fissile atoms than nitride and carbide fuel.

However, there are a lot of experiences regarding MOX because it has been used worldwide as nuclear fuel for a long time.

One disadvantage is however that its thermal conductivity is low in comparison to nitride and carbide fuel. This could become a problem at higher operating temperatures. Nitride and carbide fuels have a high density of fissile atoms and a high thermal conductivity which is good. MOX and nitride fuel have higher solidus temperatures than carbide fuel and are more preferable in that aspect as they can

---

<sup>10</sup> At lower temperatures CO<sub>2</sub> is formed instead of CO.

sustain higher temperatures. When it comes to production, the fabrication processes of nitride and carbide fuel are more difficult than for oxide fuel.

**Table 4: A comparison of different fuels.**

<b>Properties</b>	MOX fuel	Metallic fuel (U, Pu)Zr	Nitride fuel (U, Pu)N	Carbide fuel (U, Pu)C
Compatibility with coolant	+	-	+	+
Melting point	+	-	+	+/-
Solidus temperature	+		+	+/-
Thermal conductivity	-	+	+	+
Density of fissile atoms	+/-	+	+	+
Production	+		-	-

Today MOX seems to be the best choice because nitrides and carbides are difficult to produce. Nitrides and carbides however have higher densities of fissile atoms, which is preferable for fast reactors.

## 5 Corrosion in structural materials

Structural materials in LFRs are made of different types of steels. Some examples of structural materials are the steels used to hold fuel rods together as well as the core reactor tank and control rod support structures. In a LFR, corrosion on structural materials is an important issue that needs to be solved.

A lot of research has been made on short- and medium-term experiments with liquid lead. Unfortunately, the knowledge in medium- and long-term corrosion behavior, where the coolant has a velocity, is not that developed.

However, experiments show that the corrosion magnitude mainly depends on the amount of dissolved oxygen in the coolant and the temperature. Thus it is important to be able to control the oxygen concentration in the coolant in order to prevent corrosion. A lot of R&D activities are in progress on the oxygen sensor technology (see also section 4.2). Some of today's martensitic and ferritic steels corrosion compatibility with liquid Pb and LBE has been investigated on a large scale. A ferritic steel is a steel with 12-18 wt.% Cr and martensitic steel is a steel with 11-17 wt.% Cr and 0.1-0.65 wt.% carbon (27), (28).

<sup>11</sup> wt.%: A components percentage in weight.



Result shows that these steels can build up a protective oxide layer if the oxygen content is of the right concentration and if the temperature does not exceed 450 °C (29). For higher temperatures than 500 °C, the protective oxide layer seems to fail in the sense that it cannot protect the steel. Therefore new methods and materials are needed (29). One method is to use a Fe-Al coating, which has proven to strengthen the corrosion resistance on structural materials. For higher temperatures, oxide dispersive strengthened steels (ODS steels) may work, but more research is needed. One type of oxide that is used for ODS steels is Y<sub>2</sub>O<sub>3</sub> which is produced in powder form with a particle size of few tens of nanometers (30). The oxide in the ODS steel gives it more strength against mechanical creep and irradiation, and maybe also more strength against liquid metal corrosion.

Corrosion is one of the main issues for lead cooled fast reactors and there is a lot of research going on regarding this phenomenon. The liquid metal coolant wears down the steels surface and small fragments dilute into the liquid coolant.

## 5.1 The corrosion phenomenon

Corrosion is one of the main issues for lead cooled fast reactors and there is a lot of research going on regarding this phenomenon. The liquid metal coolant wears down the steels surface and small fragments dilute into the liquid coolant.

In a reactor there is a non isothermal environment, it exists a colder part and a hotter part. This leads to a transfer of steel fragments from the reactor wall's hotter part to the cooler part where they will form coatings. This may cause clogging of piping, which can lead to a decrease of heat transfer. The main reason for liquid metal corrosion is dissolution, meaning that the steel dissolves in the liquid metal coolant. The dissolution rate depends on the type of liquid metal coolant, flow rate of the coolant, content of impurities such as oxygen and nitrogen in coolant and the composition of the steel. The steels also dissolve easier in the liquid metal coolant if they have a high solubility in the coolant.

There are two forms of corrosion; uniform and local. Uniform corrosion causes a uniform damage over the surface. Local corrosion occurs where the steel has defects and is more fragile to corrosion attacks. One defect can be flaws in the crystal structure in the steel. The velocity of the liquid metal makes the corrosion accelerate; this is called flow accelerated corrosion. There are four different kinds of flow accelerated corrosion. The four types are mass transport controlled corrosion, phase transport controlled corrosion, erosion corrosion and cavitation corrosion. These four stages of flow accelerated corrosion are described below and represent different velocities of the coolant. In a low coolant velocity the mass transport controlled corrosion occurs, which is characterized by a dissolution rate that is larger than the

mass transfer rate<sup>12</sup>. This makes mass transfer the depending factor for this kind of corrosion. In a higher coolant velocity the phase transport controlled corrosion occurs, which also has mass transfer as the depending factor.

If coolant flow becomes highly turbulent, particles in the coolant can wear down the protective oxide film on the steels surface due to erosion. This phenomenon is therefore called erosion corrosion, which is a problem for liquid metal pumps (see chapter 6). Finally there is cavitation corrosion, which occurs at higher coolant velocities than for erosion corrosion. In this type of corrosion bubbles are formed in the coolant.

These bubbles collapse on the steel surface and create small micro jets, which put high pressure on local parts of the steel surface. This can lead to high stress, which in turn can lead to corrosion. All these types of corrosion are shown in figure 3.

---

<sup>12</sup> Mass transfer rate: Mass transfer rate is the speed at which the dissolved steel is transported away from the steel surface.

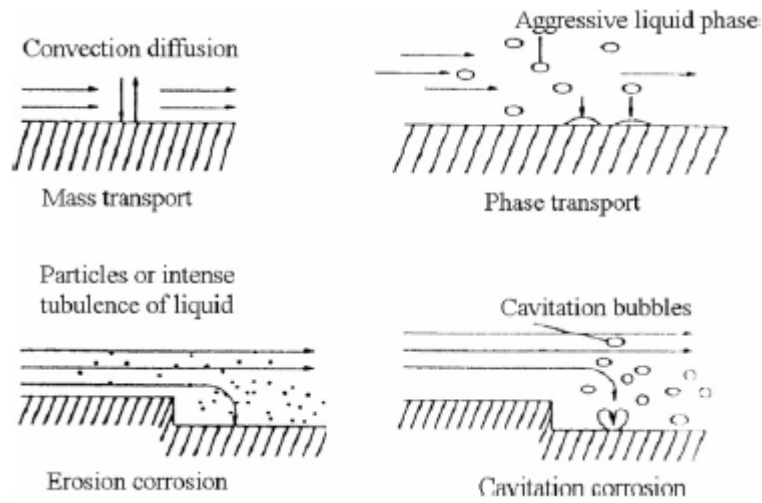


Figure 3: Four types of flow accelerated corrosion (36)

### 5.1.1 Solubility of iron, chromium and nickel in lead and LBE

In most steel alloys there are large quantities of iron, nickel and chromium. Hence, their solubility in lead and LBE plays an important role for the corrosion phenomenon. There is a connection between solubility and temperature which is described in equation (9) (36).

$$\log c_s = A_c - \frac{B_c}{T}, \quad (9)$$

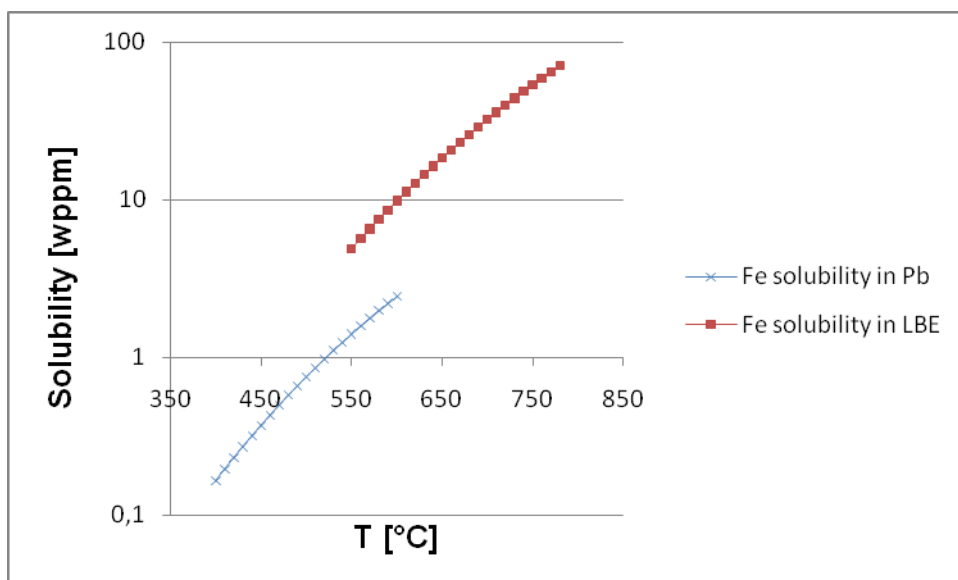
where  $c_s$  is the solubility and  $A_c$  and  $B_c$  are constants. The solubility is given in  $\text{wppm}^{13}$ .  $A_c$  and  $B_c$  are tabled in Table 5.

<sup>13</sup> Parts per million in weight.

**Table 5: Values for  $A_c$  and  $B_c$ . This function is valid in different temperature intervals for different coolants and alloy materials. All temperature intervals are given below (36).**

Metal	Coolant	$A_c$ [nu <sup>14</sup> ]	$B_c$ [K]	Valid temperature interval [°C]
Fe	Pb	4.34	3450	400-600
Fe	LBE	6.01	4380	550-780
Cr	Pb	7.88	6948	327-1244
Cr	LBE	3.98	2280	400-900
Ni	Pb	5.30	1381	327-1244
Ni	LBE	5.53	843	400-900

In figures 4-6 the solubility temperature dependence for Fe, Cr and Ni in lead and LBE are shown. The red vertical line that crosses the temperature axis in figure 4-7 marks the planned outlet temperature for commercial LFRs.



**Figure 4: Solubility of Fe in Pb and LBE as a function of temperature.**

<sup>14</sup> No unit.

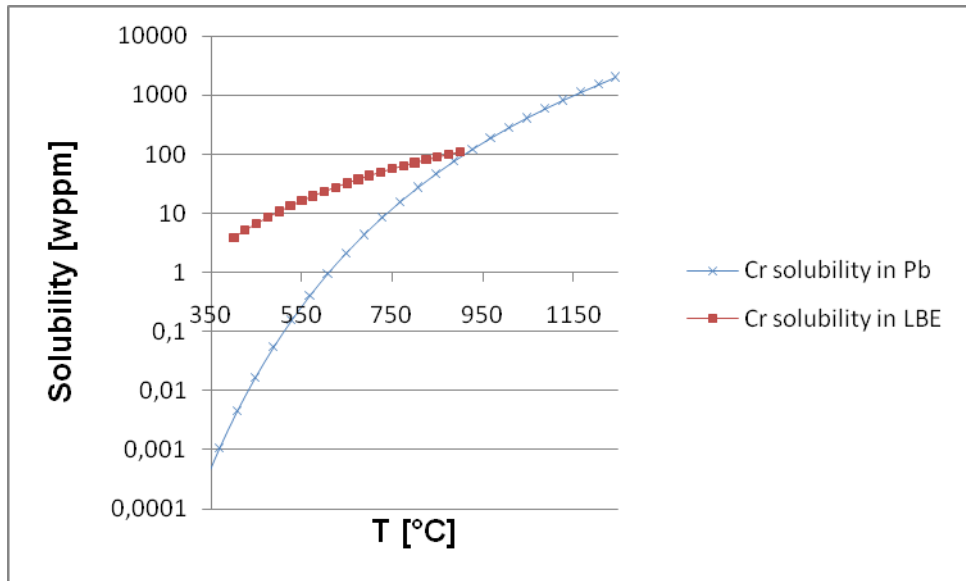


Figure 5: Solubility of Cr in Pb and LBE as a function of temperature.

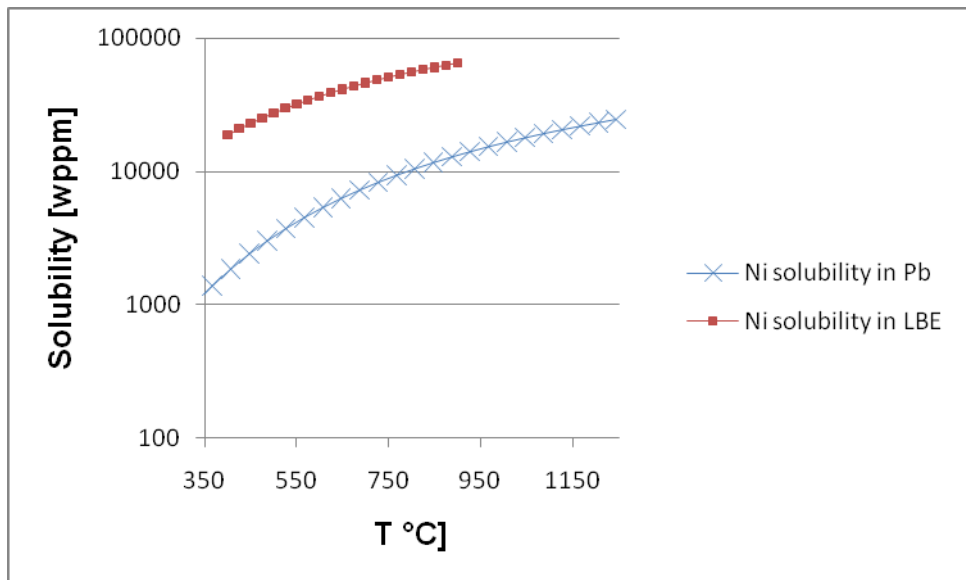


Figure 6: Solubility of Ni in Pb and LBE as a function of temperature.

The graphs 4-6 clearly show that solubility of Fe, Cr and Ni increase significantly when the temperature is increasing.

Nickel has a very high solubility in both Pb and LBE compared to Fe and Cr, which makes it unqualified as an alloy material for LFRs. To illustrate this, the solubility of Fe, Cr and Ni in lead are shown in figure 7 below.

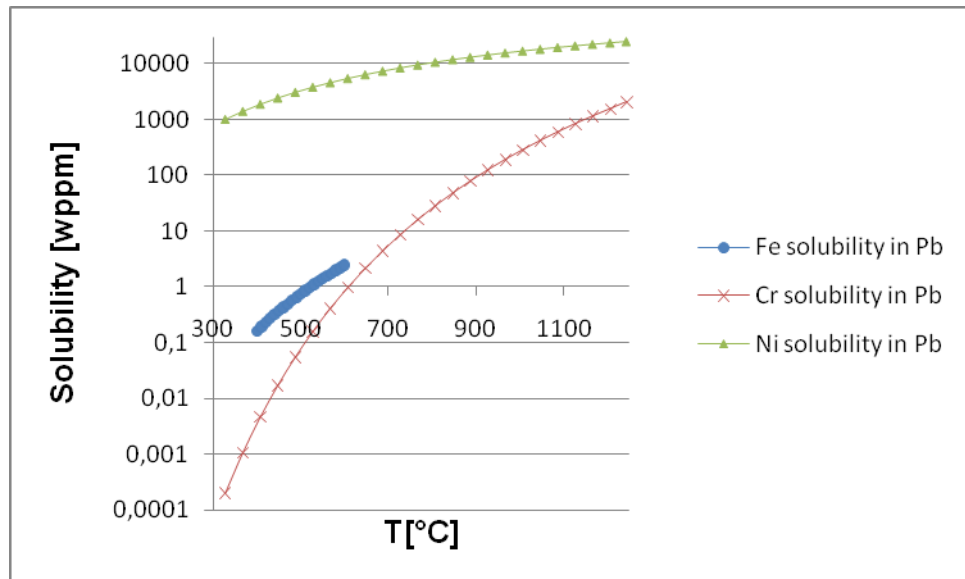


Figure 7: Solubility of Fe, Cr and Ni in pure lead.

Another important observation is that the solubility is larger in LBE than in Pb at the same temperature, which makes LBE more corrosive against structural materials. However, Pb has a higher melting point than LBE and therefore needs a higher operating temperature, which in turn leads to higher solubility. This is an important aspect that needs to be considered before a decision regarding coolant can be made.

## 5.2 Oxygen concentration in molten coolant

A protective oxide film is very effective against liquid metal corrosion. The oxygen level should be in a certain range of concentration, depending on the temperature, in order for a protective oxide layer to form. The reason for this is that lead and bismuth oxides are created in higher oxygen concentrations and they do not form a protective oxide layer, but they contaminate the coolant in form of impurities. A too low oxygen concentration is not preferable either because the protective oxides cannot be formed in a too low oxygen concentration.

The protective oxide layer is formed by a reaction with components in the structural steel and the oxygen in the coolant. A protective chromium-oxide can for example be established if the steel contains chromium

Lead and bismuth are more chemically inert<sup>15</sup> than most of the components in steels and therefore it is possible to have an environment where only desirable oxides are created. If the oxygen content is at a proper level, it is possible to maintain a self healing oxide surface on the steel. The free energy of formation can be used to illustrate which type of oxide that is easiest to form. Among the oxides, Fe<sub>3</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> are wanted because they protect the steel from corrosion. Non wanted oxides are Bi<sub>2</sub>O<sub>3</sub> and PbO because they contaminate the coolant and make it less thermal hydraulic, which decreases the heat transfer (37). In a certain range of oxygen concentration, only protective oxides are formed. If the oxygen concentration is too high PbO and Bi<sub>2</sub>O<sub>3</sub> can be created. They are formed with the excessive oxygen that remains after the formation of Fe<sub>3</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub>. In a too low oxygen concentration, the protective oxides Fe<sub>3</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> cannot be formed.

### 5.2.1 Oxygen control

One way to control the oxygen concentration in the coolant is to control the partial pressure<sup>16</sup> of the oxygen in the cover gas. The oxygen concentration in the coolant should be in equilibrium with the oxygen concentration of the cover gas because it is easier to control oxygen partial pressure in the cover gas than in the coolant. The cover gas is located above the coolant and can contain argon, oxygen and hydrogen gas (38). If the partial pressure is known, it is possible to calculate the concentration of the oxygen. A chemical reaction between oxygen and hydrogen gas is used to calculate the oxygen partial pressure. Figure 8 illustrates which oxygen partial pressure that is needed to form different oxides in different temperatures.

---

<sup>15</sup> Chemically inert: Harder to form compounds with other elements.

<sup>16</sup> Partial pressure: In a mixture of gases the partial pressure is the pressure that a single gas would have in the total gas volume.

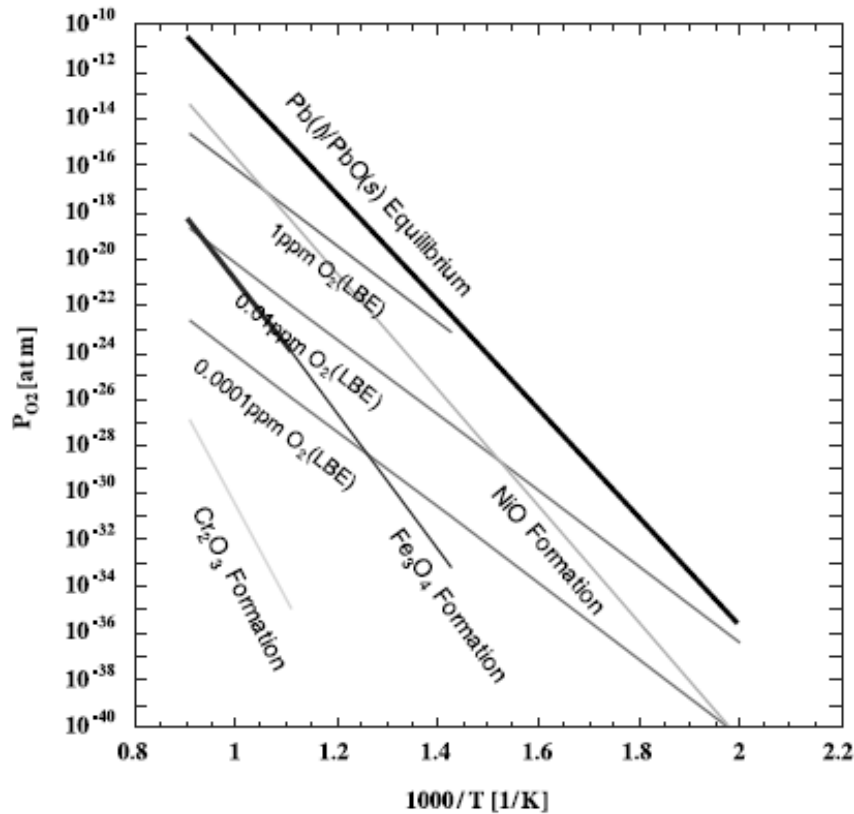


Figure 8: Oxygen partial pressures needed to form different oxides (37).

This figure also shows that higher oxygen content is required to form oxides at a higher temperature. In order to protect the steel from liquid metal corrosion in the long term, the oxide film must be self healing. Oxygen concentration cannot be left to decrease over time because then the self healing process cannot proceed.

### 5.2.2 Oxygen concentration monitoring

In order to get a more precise measure of the oxygen concentration in the coolant, oxygen sensors can be used. In liquid metal application, solid electrolytes are used. The process in this sensor is shown in figure 9. The sensor uses the difference in oxygen concentration, which creates an electromotive force (EMF) that can be measured. A larger value of the EMF indicates lower oxygen concentration in the liquid coolant and vice versa.

There is however one issue with this sensor, it only works at temperatures above 300 °C due to the lack of oxygen diffusion in the solid electrolyte (37). This issue has been solved by measuring the EMF signal in different temperatures where the sensor works.



This temperature dependence makes it possible to get information about the oxygen concentration at temperatures below the sensors temperature range.

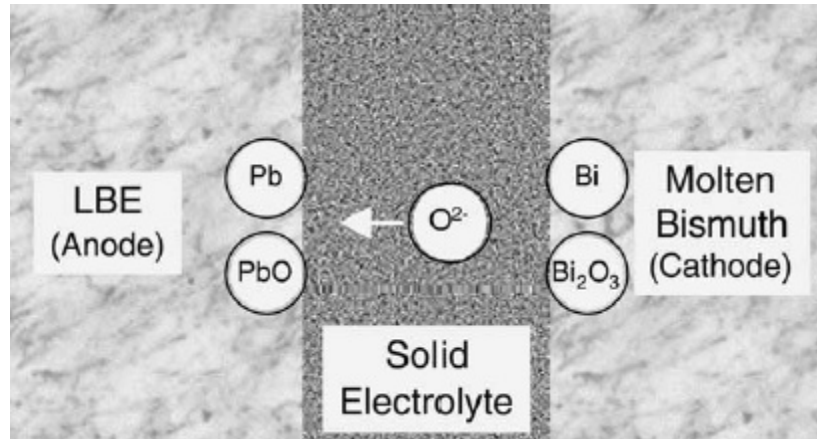


Figure 9: Picture of the process in a solid electrolyte (37).

### 5.3 Embrittlement and mechanical properties

Embrittlement is a non-desirable property in all engineering aspects. When steel becomes brittle it gets a structure that is similar to glass and thereby loses some of its ductility and strength. There is a phenomenon that is called 475 °C embrittlement which occurs to steels containing more than 12 wt.% chromium (39). This is unfortunate because chromium increases the high temperature strength. Steels, with a high Cr content, that are exposed to temperatures around 475 °C (280-500 °C) for a long time will become brittle and are not suitable for engineering applications (40). What happens is that a Fe-Cr alloy with 12 wt.% Cr or more, starts to decompose into two structural phases, one iron rich phase ( $\alpha$ -phase) and one chromium rich phase ( $\alpha'$ -phase) (40). It is the chromium rich phase that promotes embrittlement. For temperatures above 550 °C this phenomenon seems to disappear (40).

Another issue that is important to avoid is rupture, which is a mechanical property. Too high aluminum content in the steel reduces the creep rupture time<sup>17</sup>, which is not desirable. It was shown in one experiment that an addition of 4 wt.% aluminum in an alloy reduced the creep rupture time to 50% in comparison to another alloy without aluminum. Thus, the aluminum content cannot be too high (8). Aluminum also affects the weldability of the steel and that is another reason to why an alloy should not contain too much aluminum. Aluminum however strengthens the corrosion resistance because aluminum-oxide works as a protective layer (35).

<sup>17</sup> Creep rupture time: The time it takes for a material to rupture.

In Figure 10 it is shown which contents of Cr and Al that optimize the alloy properties.

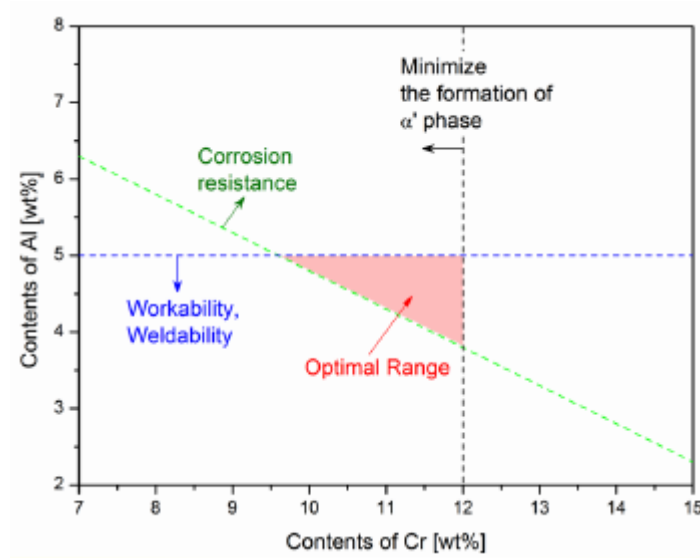


Figure 10: Optimal range of Al and Cr contents in an alloy (41).

### 5.4 Commercial structural materials available today

To see how today’s commercial steels can handle a corrosive environment some test results on different steels are presented here. All mentioned commercial steels in this report are listed in table 6. It should be noted that all tests described here are performed by the researchers referred to in the text and not by the author of this report.

Table 6: Major components of commercial steels given in wt.% (31), (32), (33).

Steel/Element	Cr	Al	Ni	Zr	Fe
316-L	16	---	10	---	Balance
SS316	16.3	---	13.9	---	Balance
HT-9	12	---	0.56	---	Balance
T-91	9	---	---	---	Balance
EP823	11.4	---	0.7	---	Balance
20Kh13	13	---	---	---	Balance

#### 5.4.1 316-L steel

Corrosion tests in liquid lead have been made on the steel 316-L at 460 °C where a single layer of protective oxide film was created and no corrosion occurred, the experiment duration was 3000 h. For higher temperatures like 550 °C corrosion was detected in 316-L after 2000 h of liquid metal interaction.

Tests with LBE have also been performed. If the oxygen amount can be maintained at a level of 10<sup>-6</sup> wt.% and the LBE flow rate has a maximum of

1 m/s at a temperature of 400 °C the oxide layer could grow to be tens of μm thick. However, this process could take several years and in the long term oxygen barrier build up rate will be less than 10<sup>-1</sup> μm per year. If the oxygen content is stable the 316-L steel could probably be used for 15 years in temperatures below 480 °C and its lifetime could go beyond 30 years at temperature around 400 °C.

Lead and LBE corrosion resistance for this kind of steel is not sufficient at higher operating temperatures than 480 °C. Note that oxygen content, according to the experiments results, has to be around 10<sup>-6</sup> wt % if 316-L steel is to be used for longer periods of time in temperatures between 400-480 °C (31).

#### 5.4.2 SS316 steel

Corrosion tests of SS316 in liquid LBE have also been performed. SS316 is common to use in the commercial nuclear reactors of today, and is therefore worth to investigate further. In this experiment the steel was pre-oxidized in order to protect it from corrosion.

The experiment took place in 550 °C stagnant molten LBE with an oxygen concentration of 1.17·10<sup>-3</sup> wt.% for 1335 h (42). When the tests were finished, it was noticed that the oxide layers had not formed continuously over the whole sample area, which can lead to LBE penetration. Cracks had also been formed within or between the oxide layers and in some places the oxide layer had spalled off. Hence, it can be concluded that the commonly used steel SS316 is not corrosion resistant, at least not at this temperature and oxide concentration.

#### 5.4.3 HT-9 steel

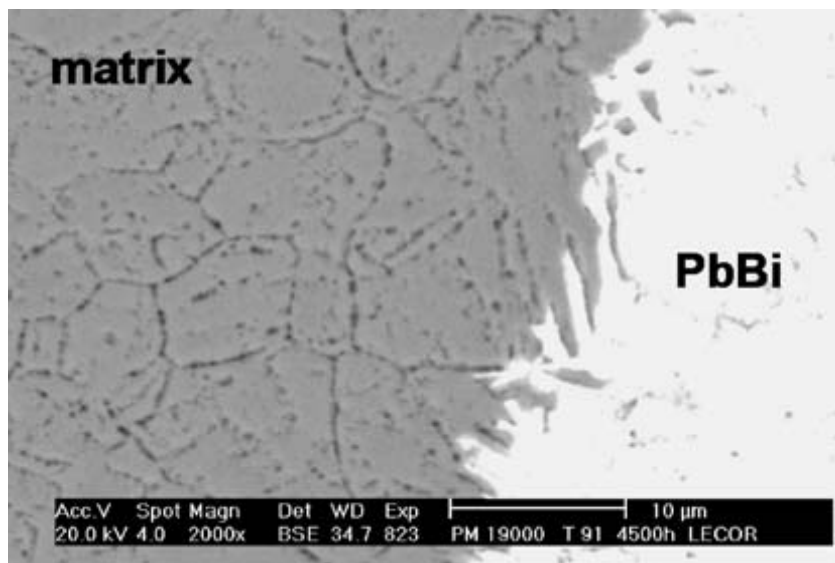
HT-9 is ferritic-martensitic steel, which does not have a good protection against corrosion from lead or LBE. An oxide layer could help to protect against the metal coolant in the same way as the previous steel type 316.

Experiments show that this steel develops a double oxide layer after 1000 h in a temperature of 450 °C (31). However, the oxide layer is too thick and will eventually

develop cracks, which leads to corrosion. HT-9 steel is therefore not suitable for long-term usage in a reactor.

#### 5.4.4 T-91 steel

T-91 is a ferritic-martensitic steel that is made to withstand high temperatures and it is used in today's conventional reactors. In a corrosion test with low concentration of oxygen ( $10^{-8}$ - $10^{-10}$  wt.%) in molten LBE at 400 °C, there was some weight loss of the steel (43). When the time of the experiment increased, the corrosion increased drastically. A higher oxygen concentration would therefore be preferable to avoid corrosion.



**Figure 11: LBE penetration in T-91 steel after 4500 h in 400 °C with an oxygen concentration of  $10^{-8}$ - $10^{-10}$  wt.%. The dark grey area is T-91 steel and the light grey is LBE. The figure illustrates corrosion at the boundary between the steel and the coolant. (43)**

If the oxygen has a concentration of 10<sup>-6</sup> wt.% this steel can be protected for at least 3000 h in a temperature of 550 °C (31).

#### 5.4.5 EP-823 steel

Russian researchers have conducted several corrosion tests on steels. One of the steel types tested is EP-823 which was used commonly in the LBE cooled reactors in the sub-marines. EP-823 was designed to be used in a lead cooled reactor with relatively low temperature. In tests with liquid LBE at 535 °C,

EP-823 showed almost no corrosion attacks in up to 600 h (31)

In another experiment with a higher temperature of 650 °C and an oxygen concentration of 2·10<sup>-5</sup> wt.% a protective oxide film was created on the steel (44). This layer consisted mostly of dichromium-trioxide. After a while, iron migrated out from the oxide film into the liquid lead, but some iron stayed in the film and created iron oxide. Another reaction also took place and formed a protective iron-dichromium-tetraoxide film. After 3500 h, this mixed oxide film still protected the steel from corrosion (9).

#### 5.4.6 20Kh13 steel

20Kh13 is widely used for blades in steam turbines and this material has a good erosion resistance. In an experiment 20Kh13 was held in stagnant molten lead with a temperature of 650 °C for 500 h. Oxygen concentration in the lead was at saturation level, which is around 6.1·10<sup>-3</sup> wt.%. The thickness of the oxide layer increased with time and the corrosion rate decreased (33).

**Table 7: Corrosion and oxide layer values (33)**

Parameter				
Time [h]	50	100	200	500
Oxide layer [μm]	12	17	25	30
Corrosion rate [mm/yr]	1.05	0.74	0.55	0.26

After 100 h of liquid lead exposure, the surface was partly covered with an oxygen layer and when 500 h had passed, the surface was still almost covered with an oxide layer (33).

The layer consisted of two sub layers, which had similar compositions. The lower layer consisted of an oxide with iron, lead and chromium while the upper oxide layer consisted of iron and lead. Lead could not penetrate the double oxide layer and therefore corrosion could only occurred at certain areas (33). This experiment had a duration of only 500 h which is rather short, and a longer time period is required to see whether the oxide layer will cover the whole sample surface.

#### 5.4.7 Summary of commercial steels

Most of today's commercial steels cannot handle corrosion in liquid lead at higher temperatures than 550 °C, but for the development of a research LFR it could be possible to use some of them for lower outlet temperatures around 450 °C (Caro, 2006). EP-823 has been used and seems to have superior corrosion resistance compared to the other steels described above (31).

## 5.5 Future steels

Today's commercial steels are not suited for usage in a commercial LFR, therefore a new kind of steel is needed.

Tests have been made on several new steels, oxide dispersion strengthened (ODS) steel is one example. An important characterization for ODS steels is the doping of oxide particles, which is supposed to make the steel more resistant to mechanical creep. Tests have shown that ODS steels have good creep strength and neutron irradiation tolerance. These steels are shown in table 8.

**Table 8: Major components of commercial steels and new steels given in wt.%. The thick line separates commercial steels from non-commercial ones (31), (32), (33), (34), (35).**

Steel/Element	Cr	Al	Ni	Zr	Fe
316-L	16	---	10	---	Balance
SS316	16.3	---	13.9	---	Balance
HT-9	12	---	0.56	---	Balance
T-91	9	---	---	---	Balance
EP823	11.4	---	0.7	---	Balance
20Kh13	13	---	---	---	Balance
ODS1	16.1	3.4	---	---	Balance
ODS2	13.7	3.4	---	---	Balance
ODS3	17.3	3.5	---	---	Balance
ODS4	15.8	1.9	---	---	Balance
ODS5	16.0	---	---	---	Balance
ODS6	16.1	3.4	---	---	Balance
ODS9	15.4	3.8	---	---	Balance
ODS14	14.9	3.7	---	0.63	Balance
12Cr steel	10.54	---	0.33	---	Balance

### 5.5.1 Corrosion tests of ODS steels with different compositions

This experiment consisted of several tests, carried out by Takaya et al., with different temperatures and oxygen concentrations in order to see how the steels were able to tolerate different environments. The temperatures of the tests were 550 °C and 650 °C and the oxygen concentrations were 10<sup>-8</sup> wt.% and 10<sup>-6</sup> wt.%. The steels were exposed to stagnant LBE for different periods of time. All exposure times are given in the tests below. The 12Cr steel is a steel that has a similar composition as today's commercial steels.

This steel was used as a reference steel in order to see how much better the ODS steels can resist liquid metal corrosion (34),(35).

#### **5.5.2 Test with $C_{O_2} = 10^{-8}$ wt.% at 550 °C**

All samples containing aluminum experienced no dissolution attacks and they also had a thin Al-oxide layer. ODS 9 and 14 had a mixed Cr-Al oxide layer of a few micrometers. ODS5 that does not contain any Al had a dissolution attack over a large part of its surface after 1000 h and after 3000 h almost the entire surface had experienced dissolution attacks. The 12Cr steel had a dissolution attack after 800 h with depth of about 1  $\mu\text{m}$ , but after 5000 h there was no significant change (34).

#### **5.5.3 Corrosion tests of ODS steels with different compositions**

This experiment consisted of several tests, carried out by Takaya et al., with different temperatures and oxygen concentrations in order to see how the steels were able to tolerate different environments. The temperatures of the tests were 550 °C and 650 °C and the oxygen concentrations were 10-8 wt.% and 10-6 wt.%. The steels were exposed to stagnant LBE for different periods of time. All exposure times are given in the tests below. The 12Cr steel is a steel that has a similar composition as today's commercial steels.

This steel was used as a reference steel in order to see how much better the ODS steels can resist liquid metal corrosion (34),(35).

#### **5.5.4 Test with $C_{O_2} = 10^{-8}$ wt.% at 550 °C**

All samples containing aluminum experienced no dissolution attacks and they also had a thin Al-oxide layer. ODS 9 and 14 had a mixed Cr-Al oxide layer of a few micrometers. ODS5 that does not contain any Al had a dissolution attack over a large part of its surface after 1000 h and after 3000 h almost the entire surface had experienced dissolution attacks. The 12Cr steel had a dissolution attack after 800 h with depth of about 1  $\mu\text{m}$ , but after 5000 h there was no significant change (34).

#### **5.5.5 Test with $C_{O_2} = 10^{-6}$ wt.% at 650 °C**

The final test had the same temperature, as in the previous test, but with higher oxygen concentration. This shows whether a higher oxygen concentration could reduce corrosion also in higher temperatures. All ODS steels containing aluminum were covered with a thin outer Al-oxide layer and they did also show resistance against dissolution. ODS5 had an oxide layer consisting of Cr, which protected it from dissolution. From this test it was shown that the higher oxygen concentration (10-6 wt.%) was better than the lower oxygen concentration option (10-8 wt.%) in order to reduce corrosion (34), (35).

### 5.5.6 Summary of the tests

In table 9 all results from the tests are shown.

**Table 9: Results from corrosion tests (34), (35).**

Test condition	Result
550 °C and $C_{O_2}^{18} = 10^{-8}$ wt. %	Only ODS 5 and 12CR steel experienced corrosion. They do not contain any Al.
550 °C and $C_{O_2} = 10^{-6}$ wt. %	Only ODS 5 experienced corrosion
650 °C and $C_{O_2} = 10^{-8}$ wt. %	Only ODS 14 that contain Zr experienced no corrosion.
650 °C and $C_{O_2} = 10^{-6}$ wt.%	No steel experienced corrosion.

In the tests it was proven that steels with an Al content of around 3.5 wt.% had the best corrosion resistance, among the tested ODS steels, except in the condition of higher temperature and lower oxygen concentration (35). Aluminum makes it possible to form a thin but very dense oxide layer, which is effective against corrosion. An addition of 13.5 – 17.5 wt.% chrome in the steel does not significantly increase the corrosion resistance if it already contains 3.5 wt.% aluminum (35). ODS14 and ODS9 have similar chemical compositions but ODS14 had better corrosion resistance in higher temperature and lower oxygen concentration. There is one considerable difference however; ODS14 contains a small amount of Zr.

Zirconium is a so called reactive element<sup>19</sup> which makes it possible to form a protective chromium oxide layer with a low amount of chromium in the steel. For aluminum oxide, zirconium seems to have no effect as a reactive element. More research is needed to determine the zirconium effect on corrosion resistance.

## 5.6 New ceramic materials

MAXTHAL (Ti<sub>3</sub>SiC<sub>2</sub>) is a ceramic with both metal and ceramic properties. Some good qualities are resistance to mechanical damage, resistance to thermal shocks and thermal and electric conductivity.

MAXTHAL's properties at 20 °C are listed in Table 10.

<sup>18</sup> Concentration of oxygen in coolant.

<sup>19</sup> Reactive element: Works as a catalyst for the formation of the oxide layer.



**Table 10: Properties of MAXTHAL (45)**

Properties	Values
Density [g/cm <sup>3</sup> ]	4.53
Melting point [°C]	> 2000
Young's modulus [GPa]	322 - 333
Shear modulus [GPa]	135
Hardness H <sub>v</sub> [GPa]	4 - 7
Thermal conductivity coefficient [W/mK]	37 - 43
Compressive strength [MPa]	720 - 1140

For possible application in an LFR, the material needs to be resistant against corrosion. This property was recently studied in an experiment and the conditions for this test are shown in Table 11 (46). Note that the conditions are similar to the above mentioned ODS tests except that the ODS steels were not tested in pure lead (see section 5.5).

**Table 11: Experiment conditions (46)**

Coolant	Temperature [°C]	C <sub>O2</sub> [wt. %]	Time of exposure [h]
Pb	550	10 <sup>-6</sup>	4000
Pb	550	10 <sup>-8</sup>	4000
Pb	600	10 <sup>-6</sup>	4000
Pb	600	10 <sup>-8</sup>	4000
Pb	750	10 <sup>-6</sup>	500 & 2000
LBE	550	10 <sup>-6</sup>	3000
LBE	550	10 <sup>-8</sup>	3000
LBE	650	10 <sup>-6</sup>	3000
LBE	650	10 <sup>-8</sup>	3000

MAXTHAL had oxidized in lead and LBE for all different temperatures and oxide concentrations in this experiment. The oxide layer consisted of an inner and an outer layer which in turn consisted of TiO<sub>2</sub> and Ti-Si-Pb-O respectively. The oxide layer thickness increased as the temperature went up. Even though the oxide films were very thin in tests with lower oxygen concentration, there were no dissolution attacks in any of the tests. Hence, MAXTHAL showed promising corrosion resistance even at higher temperatures.

## 6 Erosion in pumps

There are two types of pumps that have been discussed for usage in LFRs, mechanical and electromagnetic pumps. The electromagnetic pump has been disregarded by all LFR developers due to its low efficiency to pump liquid lead and LBE (47). Thus, mechanical pumps are discussed in this chapter.

In pumps the tip of the blades can be exposed to liquid metal with a flow velocity of 10-15 m/s. This give rise to erosion corrosion, which is an issue that has to be further investigated (48). There are no existing solution today regarding the erosion corrosion problem for pumps; however some potential solutions do exist:

- Aluminized steel impeller
- Steel impeller protected by MAXTHAL coating
- Steel impeller protected by tantalum coating
- Impeller made of solid MAXTHAL(48)

In a dedicated test with liquid metal coolant, MAXTHAL was exposed to liquid lead with an oxygen concentration of 10<sup>-6</sup> wt.% at 500 °C with a flow velocity of 1 m/s for 2000 h. No dissolution was detected (49). However, tests with higher velocities are needed to decide if MAXTHAL is a material suited for pumps in LFRs.

Regarding pump design, an axial flow pump has been proposed for ELSY (European Lead SYstem) (48), which is a project that started in 2006 (50). The reactor has not been built yet. These axial flow pumps shall be fed from the bottom. The pump assembly will hang from the reactor core roof and be able to be removed as one piece (48). As mentioned earlier, more research regarding pumps must however be done before a final decision can be made on pumps for LFRs.

## 7 Discussion

### 7.1 Reactor coolants

LBE forms hazardous polonium and no polonium extraction technology exists today. Even if such a technology would be invented, bismuth is more expensive in comparison to pure lead. LBE is therefore not preferable in lead-cooled fast reactors. LFRs are planned to have high operating temperatures and pure lead can therefore be used with a low risk of coolant freezing.

The solubility is larger in LBE than in pure lead at the same temperature, which makes LBE more corrosive against structural materials. The solubility increases in higher temperatures. LBE can be used in lower temperatures than pure lead because its melting point lies under the one for pure lead. Commercial LFRs however, are planned to have an outlet temperature of 800°C, where LBE is more corrosive against structural material than pure lead. Thus, pure lead should be the most preferable coolant regarding corrosion in planned operating temperatures of commercial LFRs.

The densities of lead and LBE decrease with higher temperatures.

This temperature depending density makes it is possible to have natural circulation in the coolant. If the reactor vessel's geometry does not support full natural convection, pumps could be used to support the coolant circulation.

## **7.2 Fuels**

Regarding fuels for LFRs, several different types have been considered. All of them except the metallic option can be used in LFRs. When nitride production can be performed on an industrial scale, nitride fuel would probably be the best choice for LFRs due to its desirable properties. One thing that has not been mentioned in this report is the cladding material for the fuel pins.

It is important that fuel cladding does not get cracks because of the hot fuel. This may be a relevant factor regarding the choice of fuel for LFRs.

## **7.3 Corrosion**

The duration of all corrosion tests described in this report were only 5000 h or less. Several materials showed good corrosion resistance in these tests, but the test durations may have been too short in order to get valid results.

Three commercial steels, EP823, 20Kh13 and T-91, exhibit corrosion resistance at 550°C with a oxygen concentration of 10<sup>-6</sup> wt.%. The planned outlet temperature of a commercial LFR is however 800°C and therefore new types of steels are needed. One new type is the ODS steel. An ODS steel with aluminum and zirconium can be used for longer tests due to its corrosion resistance in high temperatures and low oxygen concentrations. Aluminum content should not be more than 5 wt.% in an alloy because of decreased weld ability and reduced strength.

All summarized test results, except for MAXTHAL, were from tests with stagnant coolant. The coolant in a reactor is non-stagnant and therefore more tests should be performed with flowing liquid coolant, where erosion corrosion can occur.

## 7.4 Pumps

Pumps in an LFR will be exposed to high velocity of liquid metal, which induce the problem of erosion corrosion.

There are no appropriate solutions for pumps today, but there exist materials, such as MAXTHAL, that have the potential to overcome the erosion corrosion problem. In one test at 500 °C, where the liquid coolant had a velocity of 1 m/s, no dissolution was detected. MAXTHAL could be used as coating material if no other steels can withstand corrosion attacks in flowing coolant. The structures could not be made of solid MAXTHAL because it would not be economic, due to the high cost of MAXTHAL. More tests at higher temperatures and at different coolant velocities are needed though. Maybe 20Kh13 steel can be used as pump material in an early test reactor with lower operating temperature, because of its good erosion resistance.

## 7.5 Further work

If more work was to be done, it would be a good idea to study nitride fuels and pumps further. Nitride fuels are interesting due to their physical properties that are desirable for fast reactors, but the production is complex. Hence, it would be important to investigate the potential development of nitride fuel production. Further efforts could be devoted to trying to find more information about liquid metal pumps; however the information available seems to be rather limited.

Another interesting aspect that is worth studying is the economical differences between SFRs (Sodium-cooled Fast reactors) and LFRs, which are the two most promising fast reactor concepts. The significant difference between these two concepts is that the SFRs need an intermediate system for the sodium loop in order to avoid sodium-water interaction. This intermediate system is not needed in LFRs and therefore they are probably cheaper to build. A study regarding this possible economical difference could be of interest for a lot of people working with the Generation IV concept.

Two other important areas where more research is needed are the irradiation and the creep on ODS steels.

Steels in a reactor must tolerate both creep and irradiation, thus more research and experiments should be performed regarding these effects on ODS steels.

## 8 Conclusions

This study has examined different aspects related to lead-cooled fast reactors (LFRs). The goal was to identify the key issues with the LFR concept, which turned out to be corrosion on structural materials, erosion on pumps and choice of fuel.

- An ODS steel with aluminum and zirconium has shown good results in tests with LBE and could probably be used as structural material in commercial LFRs
- There is no solution regarding erosion on pumps, but a new ceramic material MAXTHAL shows promising results in tests with liquid lead of low velocity
- Nitride fuel has desirable properties but its production is more difficult than for MOX fuel. Thus, MOX fuel is the best choice as long as the production of nitride fuel has not been facilitated.

More studies regarding MAXTHAL as pump material and irradiation and creep damage on ODS steels are recommended in order to overcome the material issues with LFRs.

## 9 Acknowledgement

The author of this work would like to thank Vattenfall Research and Development AB for financial support, and the following persons:

Hans Henriksson

Anna-Maria Wiberg

My supervisor at Uppsala University, Henrik Sjöstrand, has also been of great importance for this thesis work.

Special thanks to Jesper Ejenstam, Mikael Jolkkonen and Janne Wallenius, all from KTH, because of their help with guiding and tips on where to find valuable sources of information.

## 10 References

1. **Wallenius, Janne.** *KTH Reactor Physics*. [Online] September 2010. [Cited: October 22, 2010.] <http://new.neutron.kth.se/leader/workshop/files>.
2. *www.gen-4.org*. [Online] December 2002. [Cited: October 22, 2010.] <http://www.gen-4.org/Technology/roadmap.htm>.
3. **Reynolds, Albert B. and Waltar, Alan E.** *Fast Breeder Reactors*. Virginia & Washington : U.S. Department of Energy, 1981.
4. **Nordling, Carl and Österman, Jonny.** *Physics Handbook*. Poland : Studentlitteratur AB, 2006.
5. *MYRRHA Science Towards Sustainability*. [Online] 2010. [Cited: October 26, 2010.] [http://myrrha.sckcen.be/RD/Fuel\\_qualification](http://myrrha.sckcen.be/RD/Fuel_qualification).
6. **Smith, William F. and Hashemi, Javad.** *Foundations of Materials Science and Engineering*. New York : McGraw-Hill, 2006.
7. **Tucek, K. Carlsson, J. and Wider, H.** *Comparison of sodium and lead-cooled fast reactors regarding severe safety and economical issues*. Beijing : s.n., 2005. 13th International Conference on Nuclear Engineering. p. 3.
8. **Kimura, A., et al.** *Super ODS Steels R&D for Fuel Cladding of Gen-IV Systems*. New Jersey : s.n., 2010. Innovative Materials Immune to Radiation. pp. 1-58.
9. **Zhang, Jinsuo and Li, Ning.** A review of steel corrosion by liquid lead and lead-bismuth. *Corrosion Science Vol. 51*. 2009, pp. 1207-1227.
10. **Todreas, N. and Macdonald, P.E.** *Design of an actinide burning, lead or lead-bismuth cooled reactor that produces low cost electricity*. Idaho : Idaho National Engineering and Environmental Laboratory, 2000.
11. **The OECD Nuclear Energy Agency.** Independent evaluation of the MYRRHA project. *Nuclear Science*. 2009, p. 7.
12. *MYRRHA Science Towards Sustainability*. [Online] 2010. [Cited: November 3, 2010.] <http://myrrha.sckcen.be/en>.

13. **Abderrahim, H. Aït, Aoust Th., et al.** MYRRHA, a Pb-Bi experimental ADS: specific approach to radiation protection aspects. *Radiation Protection Dosimetry vol. 116*. 2005, pp. 433-441.
14. **Jongen, Ph. Benoit and Y.** MYRRHA: A multipurpose accelerator driven system for research and development. 2003, IAEA TECDOC 1348, pp. 163-183.
15. **Jolkkonen, M.** *Nitride fuels for Gen-IV reactors*. Uppsala : s.n., 2010. GENIUS.
16. **Patterson, Charles.** *Processes going on in Nonfailed Rod during Normal Operation Volume I*. California : Advanced Nuclear Technology International, 2010.
17. **Sundaram, C. V. and Mannan, S. L.** Nuclear fuels and development of nuclear fuels elements. *Sādhanā Vol 14*. June 1989, pp. 21-57.
18. **IAEA.** *IAEA-TECDOC 1374, Development status of metallic, dispersion and non-oxide advanced and alternative fuels for power and research reactors*. Vienna : IAEA, 2003.
19. **Rogozkin, B.D. Stepennova, N.V. et al.** Mononitride U-Pu mixed fuel and its electrochemical reprocessing in molten salts. 2003, IAEA TECDOC 1348, p. 64.
20. **Crawford, T.R. Allen and D.C.** Lead-cooled fast reactor systems and the fuels and materials challenges. *Science and Technology of Nuclear Installations*. 2007, pp. 4-5.
21. **Bernard, H. P. Bardelle and Warin, D.** *Mixed nitride fuels fabrication in conventional oxide line*. 1988, IAEA TECDOC 466, p. 45.
22. **Rogozkin, B.D. Stepennova, N.M. and Proshkin, A.A.** Mononitride fuel for fast reactors. *Atomic Energy, Vol. 95, No 3*. 2003, pp. 624-636.
23. **Sjöstrand, H.** [interv.] February 8, 2011.
24. **B.D. Rogozkin, N.V. Stepennova. et al.** Mononitride U-Pu mixed fuel and its electrochemical reprocessing in molten salts. 2003, IAEA TECDOC 1348, p. 64.
25. **Frost, B.R.T.** The carbides of uranium. *Journal of Nuclear Materials vol 10*. 12 June 1963, p. 265-300.
26. **Matzke, Hj.** *Science of Advanced LMFBR Fuels*. Amsterdam : North-Holland Physics Publishing, 1986. pp. 118-233.

27. **Metalinfo.** Metals. *About.com*. [Online] 2002. [Cited: January 16, 2011.] <http://metals.about.com/library/bldef-Ferritic-Steel.htm>.
28. **Metalinfo.** Metals. *About.com*. [Online] 2002. [Cited: January 16, 2011.] <http://metals.about.com/library/bldef-Martensitic-Stainless-Steels.htm>.
29. **Smith, C.F. Cinotti, L. and Sekimoto, H.** *Lead-cooled fast reactor (LFR) ongoing R&D and key issues*. Paris : s.n., 2009. GIF Symposium . pp. 181-190.
30. **Verhiest, K., et al.** Development of oxides dispersion strengthened steels for high temperature nuclear reactor applications. *Journal of Nuclear Materials Vol. 385*. 2009, pp. 308-311.
31. **Caro, M.** *LFR Demonstrator Materials Viability*. California : University of California, Lawrence Livermore National Laboratory, 2006.
32. **Cheng, E. T. and Saji, G.** Activation and waste management considerations of fusion materials. *Journal of Nuclear Materials Vol. 212-215*. 1994, pp. 621-627.
33. **Eliseeva, O. I. and Tsisar, V. P.** Corrosion of 20Kh13 steel in lead melts saturated with oxygen. *Materials Science Vol. 41*. 2005, pp. 603-608.
34. **Takaya, S., et al.** Corrosion of Al-alloying high Cr-ODS steels in lead-bismuth eutectic. *Journal of Nuclear Materials Vol. 386-388*. 2009, pp. 507-510.
35. **Takaya, Shigeru, Furukawa, et al.** Corrosion of Al-alloying high Cr-ODS steels in stagnant lead-bismuth. *Journal of Nuclear Materials Vol. 398*. 2010, pp. 132-138.
36. **Zhang, Jinsuo and Li, Ning.** Review of the studies on fundamental issues in LBE corrosion. *Journal of Nuclear Materials Vol. 373*. 2008, pp. 351-377.
37. **Li, Ning.** Active control of oxygen in molten lead-bismuth eutectic systems to prevent steel corrosion and coolant contamination. *Journal of Nuclear Materials Vol. 300*. 2002, pp. 73-81.
38. **Tarantino, M.** *Integral Circulation Experiment: Thermal-Hydraulic Simulator of a LFR Primary System*. s.l. : ENEA, 2010.
39. **Kobayashi, Satoru. K and Takayuki, T.** Mapping 475 C embrittlement in ferritic Fe-Cr-Al alloys. *Scripta Materialia Vol. 63*. 2010, pp. 1104-1107.



40. **Sahu, J. K., Krupp, U. Ghosh, R. N. et al.** Effect of 475 C embrittlement on the mechanical properties of duplex stainless steel. *Materials Science and Engineering A Vol.508*. 2009, pp. 1-14.
41. **Il Soon, H. Lim, J. Seung, G.L. et al.** *Development of Alumina Forming Ferritic Steels for Lead-Bismuth Eutectic Cooled Applications*. Daejeon, Republic of Korea : Nuclear Transmutation Energy Research Center of Korea, 2010. OECD Nuclear Energy Agency International Workshop on Structural Materials for Innovative Nuclear Systems. pp. 1-34.
42. **Chen, X. Stubbins, J. F. Hosemann, P. et al.** Analysis of corrosion scale structure of pre-oxidized stainless steel 316 in molten lead bismuth eutectic and the relation to impedance spectroscopy response. *Journal of Nuclear Materials vol. 398*. 2010, pp. 172-179.
43. **Benamati, G. A. Gessi and G. Scaddozzo.** Corrosion behaviour of steels and refractory metals in flowing Lead-Bismuth Eutectic at low oxygen activity. *Journal of Materials Science vol. 40*. 2005, pp. 2465-2470.
44. **Eliseeva, O. I. V. P. Tsisar, V.M. Fedriko. et al.** Changes in the phase composition of an oxide film on EP-823 steel in contact with stagnant lead melt. *Materials Science Vol.40*. 2004, pp. 260-269.
45. **Górny, Gabriela, et al.** Ceramic composite Ti<sub>3</sub>SiC<sub>2</sub>-TiB<sub>2</sub>-Microstructure and mechanical properties. *Materials Characterization V. 60*. 2009, pp. 1168-1174.
46. **Heinzel, A., Müller, G. and Weisenburger, A.** Compatibility of Ti<sub>3</sub>SiC<sub>2</sub> with liquid Pb and PbBi containing oxygen. *Journal of Nuclear Materials Vol. 392*. 2009, pp. 255-258.
47. **Cinotti, L. Smith, C. F. Artioli, C. et al.** *Handbook of Nuclear Engineering*. s.l. : Springer Science and Business Media, 2010.
48. **Cinotti, L.** Mail from Luciano Cinotti. December 1, 2010.
49. **Utili, M., et al.** Ti<sub>3</sub>SiC<sub>2</sub> as a candidate material for lead cooled fast reactor. *Nuclear Engineering and Design*. July 8, 2010, pp. 1-6.
50. **Alemberti, A.** *ELSY The European Lead Fast Reactor*. Kyoto, Japan : Ansaldo Nucleare, 2009. FR09 - International Conference on Fast Reactors and Related Fuel Cycles.



### Appendix 1, MYRRHA vessel configuration

MYRRHA (Multi-purpose HYbrid Research Reactor for High-technology Applications) is planned to be a flexible lead-cooled fast reactor that can work in both a subcritical and critical mode. It is planned to be in full operation by 2020 and to be used as an accelerator-driven reactor system for the first years. This is to demonstrate the technology required for the spallation neutron source, the accelerator driver and the coupling between neutron source and reactor core. In current design plans for MYRRHA it will have a thermal power of 57 MW(11). When it comes to fuel, mixed oxide fuel (MOX) consisting of plutonium-uranium oxide is the main candidate. Design parameters for this reactor are shown in Table A.

**Table A: Dimension parameters for MYRRHA (14)**

<b>Dimensions</b>	<b>Values</b>
Core external diameter	0.9 m
Core height	1.3 m
Fuelled length	0.5 m
Vessel diameter	4-5 m
Vessel total height	7 m
Vessel cover thickness	1-2 m
Gas plenum above the coolant (if any)	0-0.5 m thickness

The planned MYRRHA vessel configuration is shown below. These figures show different angles, to indicate different parts of the reactor.

Here follows an explanation to some of the technical terms that are mentioned in pictures A-C (14):

- In-vessel fuel storage: Spent fuel is supposed to be stored here because it still generates decay heat.
- Diaphragm: Separates the lower and upper part of the vessel.
- Core barrel: Surrounds the core.
- In-pile sections: In these in-pile sections (IPS) it is possible to perform tests on samples like steel, fuel or transmutation specimens. Irradiation tests on

these samples can occur at different temperatures than the operating temperature of MYRRHA.

- Particles beam tube: Tube where protons are transported to the spallation target (LBE in this case).

Some other parts are also mentioned in the figures, such as Irradiation position, spallation source, manipulator arm and handling tool rotating plug.

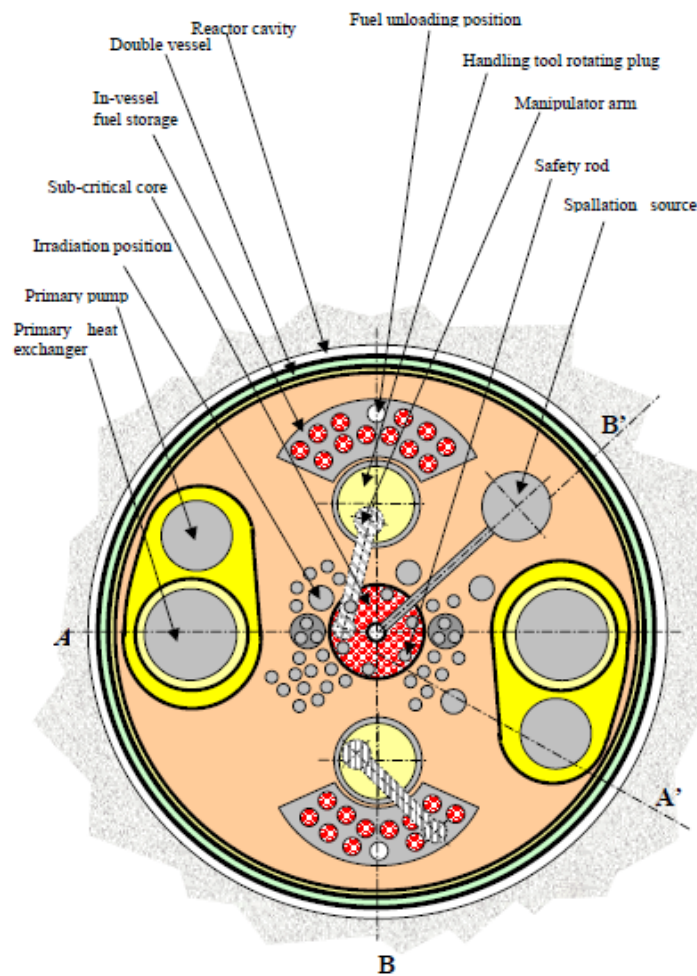


Figure A: MYRRHA vessel configuration (14)

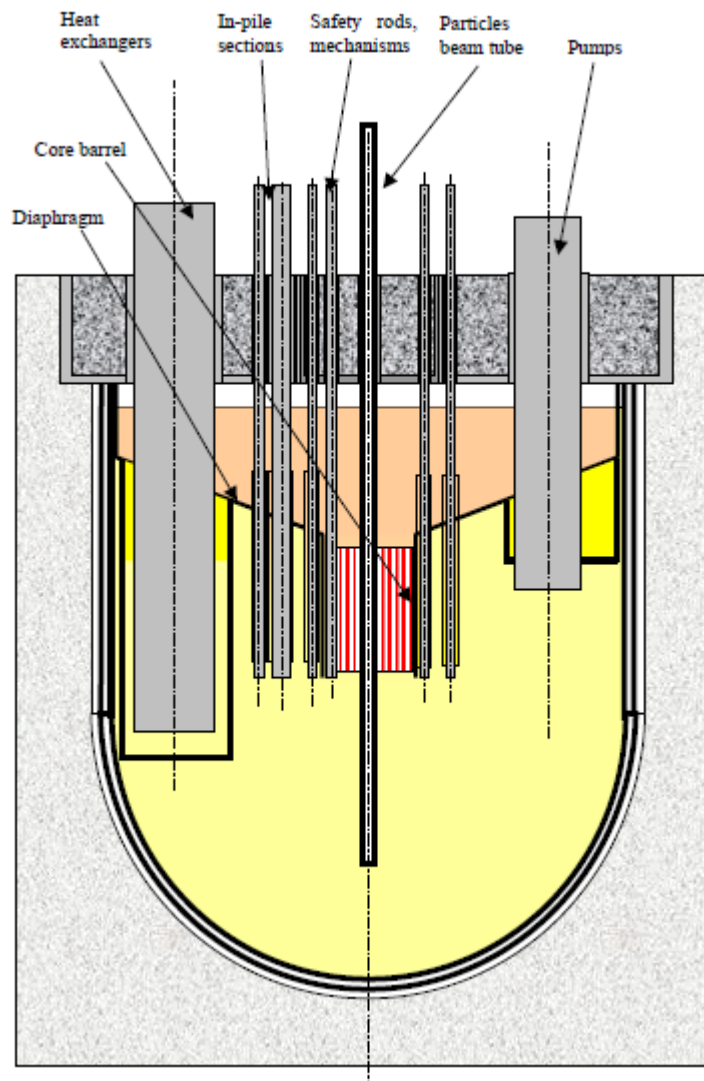


Figure B: MYRRHA vessel configuration – AA' view (14)

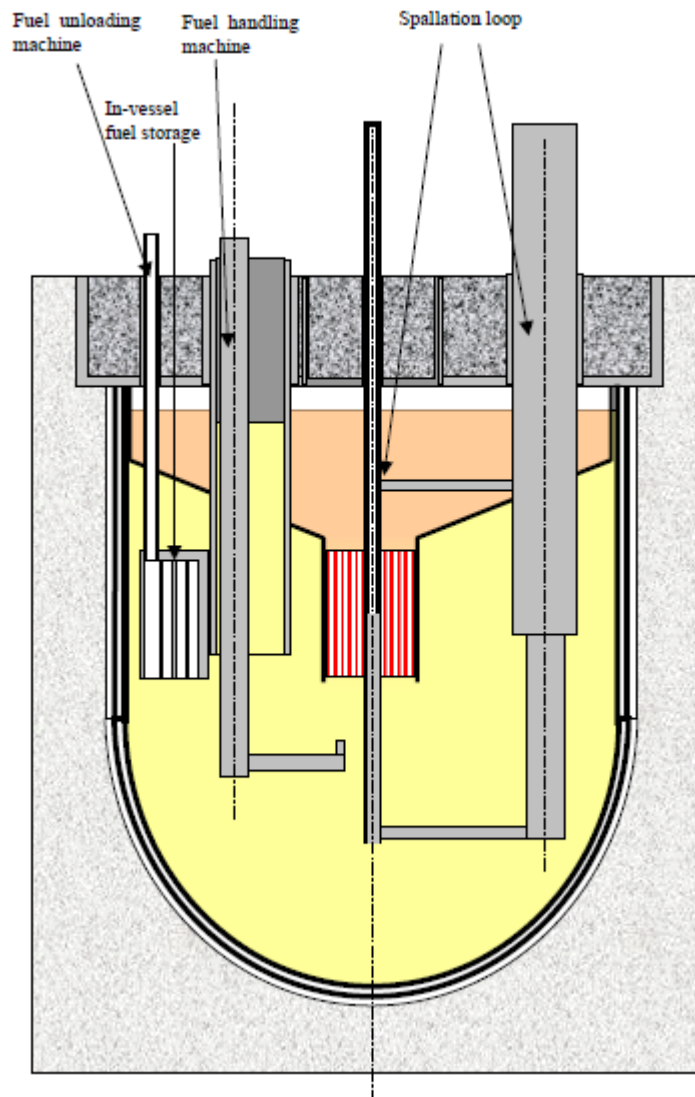


Figure C: MYRRHA vessel configuration – BB' view (14)

## Appendix 2, Chemical formulas for oxide layers

Here some different oxides are explained in form of formulas and their chemical compositions.

Dichromium-trioxide

Formula:  $\text{Cr}_2\text{O}_3$

Chemical reaction:  $4\text{Cr} + 3\text{O}_2 \rightarrow 2 \text{Cr}_2\text{O}_3$

Iron oxide

Formula:  $\text{FeO}$

Chemical reaction:  $2\text{Fe} + \text{O}_2 \rightarrow 2\text{FeO}$

Iron-dichromium-tetraoxide

Formula:  $\text{FeCr}_2\text{O}_4$

Chemical reaction:  $\text{FeO} + \text{Cr}_2\text{O}_3 \rightarrow \text{FeCr}_2\text{O}_4$

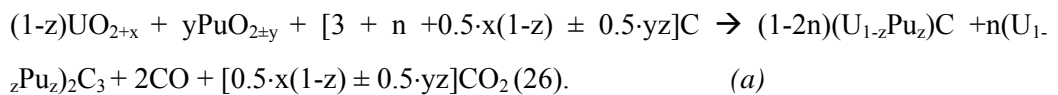




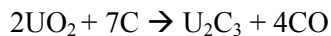
### Appendix 3, Formulas for carbide fuels

Here follows some chemical formulas for different carbide fuels.

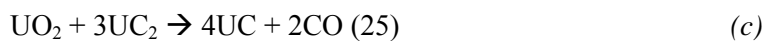
There is a general formula that can be used to express several different formulas for different sesquicarbides (see (a)). A sesquicarbide is a carbide with the form  $(U_{1-z}Pu_z)_2C_3$  where  $0 \leq z \leq 1$ .



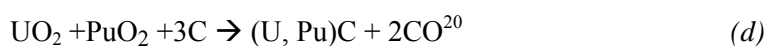
To get  $U_2C_3$  set  $x = 0$ ,  $y = 0$ ,  $z = 0$  and  $n = 0.5$ , after insertion in the reaction and after some simplifications the result is:



The remaining fuels have following chemical formulas.



The optimum temperature for these two reactions are not decided, some say 1400-1500°C and other experiments show 1800 °C or above (25).



This reaction occurs in 1400-1550 °C for 4 h (26).

---

<sup>20</sup> At lower temperatures  $CO_2$  is formed instead of CO.