Chapter 3

THERMODYNAMIC RELATIONSHIPS AND HEAVY LIQUID METAL INTERACTION WITH OTHER COOLANTS*

3.1 Introduction

This chapter collects some thermodynamics data of Pb and Pb-Bi alloys and some solubility and diffusivity values of various elements in liquid Pb and LBE. Moreover, the interaction of liquid Pb and LBE with some coolant candidates such as water, sodium or oil is also considered.

3.2 Enthalpies, entropies (solid and liquid state) – free energy and entropy of mixing

The heats of formation of six solid Pb-Bi alloys have been measured at 400 K in a liquid lead solution calorimeter by P. Roy, *et al*. They found that these alloys obey Kopp's law of additivity and the heats of formation are therefore temperature independent. The lead and bismuth used in these experiments were reported to be of 99.999% pure. With their results, they calculated integral free energies and entropies of formation for solid Pb-Bi alloys at 400 K as a function of the Pb content.

The main thermodynamic functions of interest are enthalpy *H*, free energy *F*, Gibbs potential Φ and entropy *S*. The thermodynamic functions of pure substances in the "standard condensed state" can be presented as follows:

$$H(T) = H(0) + \int_0^{T_m} C_p(T)dT + \Delta H_m(T_m) + \int_{T_m}^{T} C_p(T)dT \tag{3.1}$$

$$S(T) = \int_0^{T_m} \frac{C_p(T)}{T} dT + \frac{\Delta H_m(T_m)}{T_m} + \int_{T_m}^{T} \frac{C_p(T)}{T} dT \tag{3.2}$$

(For the considered systems it was supposed that $S^0(0) = 0$ in agreement with the third law of thermodynamics.)

$$\Phi(T) = H(T) - T \cdot S(T) \tag{3.3}$$

Usually the values of the thermodynamics functions are tabulated using the temperature of 298.15 K and the pressure of $1.01325 \cdot 10^5$ Pa as the reference standard state (STP).

The most important results of enthalpy measurement (often based on the measurement of the heat capacity) of bismuth, lead and LBE issued before 1968 were compiled and analysed by R. Hultgren,

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et al. (1973, 1974). Based on the selected sources, they provided the tables with the recommended values of enthalpy, entropy and isobaric specific heat for condensed and gas phases in a large temperature range starting from the standard temperature of 298.15 K to the normal boiling temperature. As the maximum temperature in the considered experiments was limited to about 870 K for Bi, 1270 K for Pb, the recommended data at higher temperatures were obtained by extrapolation. There is no measurement of the LBE enthalpy. Therefore it is proposed to use the Kopp's law (see also Section 2.13.3 of Chapter 2) for its estimation at temperatures higher than the lead melting point.

A detailed table with the recommended values of enthalpy, entropy and heat capacity of lead was also given by L. Gurvich, *et al*. These data were obtained by fitting of the theoretical formulae to the available experimental results and then using them for estimation of the considered properties in the whole temperature range (from 298.15 K to T_{melt}).

In the later compilation of B. Cheynet (1996) the standard values of entropy of Pb and Bi ($S_{c\,\mathrm{Pb}}(298)$ = 64.785 J mol^{-1} K^{-1}) were given together with the enthalpy tables for the range of 400-2000 K. For the liquid lead these recommendations differ for less than 0.2% from those of R. Hultgren up to 1900 K. Closer to the boiling point the difference increases to about 0.4%. For the bismuth, the results in the two works are practically identical (difference less than 0.08%).

The temperature dependence of the molten Pb and Bi enthalpies given in the references cited above are described, with deviation less than 0.5%, by the following parabolic correlations:

$$\Delta H_{\mathrm{Pb}}^{(298)}(T) = -5.133\cdot 10^{-4}\cdot T^2 + 30.3623\cdot T - 4671.91 \tag{3.4}$$

$$\Delta H_{\mathrm{Bi}}^{(298)}(T) = -5.425\cdot 10^{-4}\cdot T^2 + 28.8471\cdot T - 2592.02 \tag{3.5}$$

The enthalpy of LBE obtained using Eqs. (3.4), (3.5) and Kopp's law (for LBE composition of 44.29 at.% Pb and 55.71 at.% Bi) can be presented as follows.

$$\Delta H_{\mathrm{LBE}}^{(298)}(T) = -5.296\cdot 10^{-4}\cdot T^2 + 29.5182\cdot T - 3513.20 \tag{3.6}$$

So as to be consistent with Chapter 2 of this handbook, the enthalpy was also calculated with Eq. (3.1) above and the recommended correlations for heat capacities of the molten Pb, Bi and LBE presented in Chapter 2. This transformation yields the following relationships:

$$H(T) - H(T_m) = 33.756\cdot(T - T_m) - 3.131\cdot 10^{-3}\cdot(T - T_m)^2 + 5.7614\cdot 10^{-7}\cdot(T - T_m)^3 \tag{3.7}$$

$$H_{\mathrm{Bi}}(T) - H_{\mathrm{Bi}}(T_m) = 24.7014\cdot(T - T_m) + 6.200\cdot 10^{-4}\cdot(T - T_m)^2 - 1.5011\cdot 10^{6}\cdot\left(T^{-1} - T_m^{-1}\right)^{-1} \tag{3.8}$$

$$H_{\mathrm{LBE}}(T) - H_{\mathrm{LBE}}(T_m) = 33.1025\cdot(T - T_m) - 5.6628\cdot 10^{-3}\cdot(T - T_m)^2 + 1.4823\cdot 10^{-6}\cdot(T - T_m)^3 \tag{3.9}$$

All the literature data together with the recommended curves based on Eqs. (3.7) and (3.8) are presented in Figures 3.2.1 and 3.2.2. Figure 3.2.3 presents the results of calculation of the LBE enthalpy together with those for Pb and Bi. The maximum deviation of the presented literature data from the proposed recommended curves does not exceed 1.6% for Bi and 5% for Pb.

Figure 3.2.1. Variations of the lead enthalpy with temperature

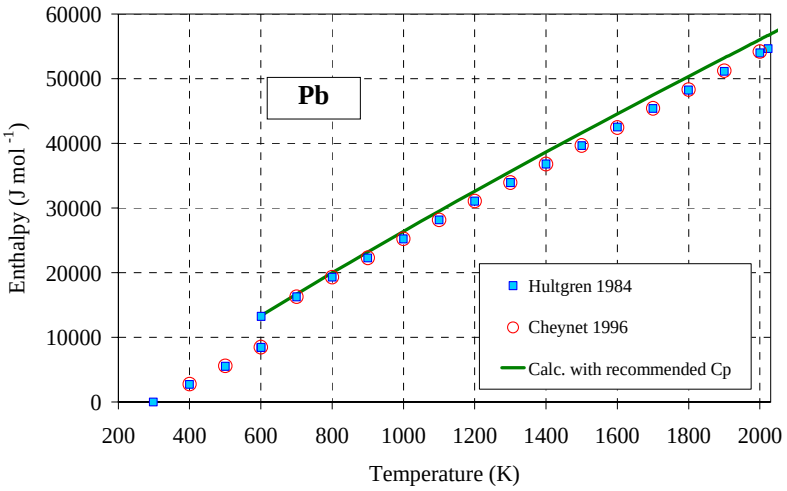


Figure 3.2.2. Variations of the bismuth enthalpy with temperature

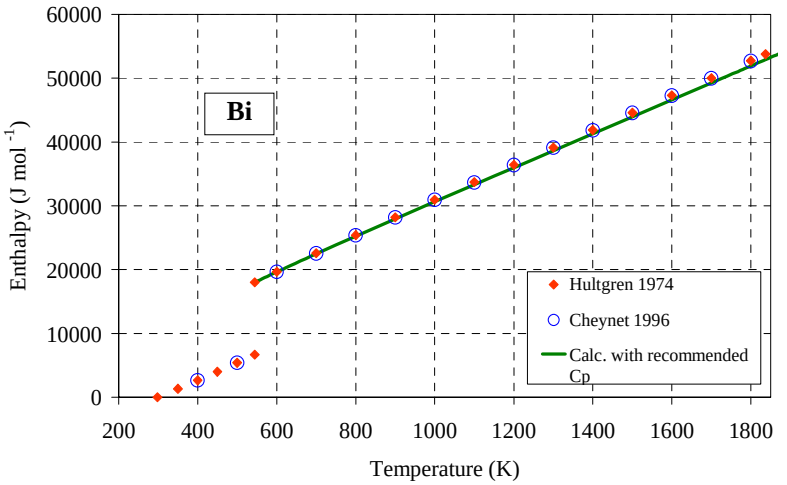
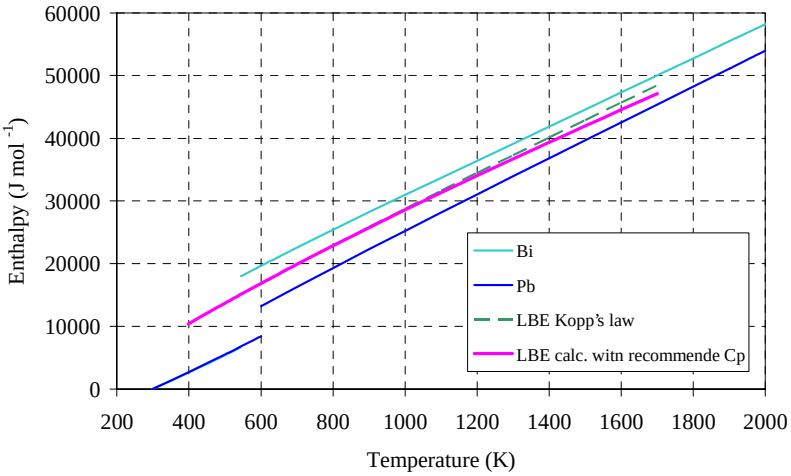


Figure 3.2.3. Calculated values of the LBE enthalpy



3.3 Purity requirements

The chemical composition of lead or LBE is of importance for the operating conditions of a nuclear system:

- First, the formation of radioactive elements due to irradiation induces a contamination of the circuits and components. It may also have an influence on physical parameters of the reactor.
- Second, a high content of some impurity elements in the coolant may have an effect on the coolant chemistry control and affecting the corrosion resistance of structural steels.
- Third, if some impurities react with other elements produced under irradiation, it can induce solid precipitation at the surface of the primary circuit components and may strongly affect thermal and hydraulic characteristics of the reactor. Moreover, mass transfer from a thermal gradient for example can induce precipitation of solids in the coldest parts of the circuit which may result in flow blockages or instabilities.

The main sources of impurities in the heavy metal coolant in nuclear systems are:

- metallic impurities due to the limits of the refining process and their ingress during casting;
- corrosion and erosion products resulting from the interaction of structural materials with the heavy liquid metal coolant;
- coolant interaction with gas in the circuit;
- spallation or fission products due to proton or neutron beam/material interactions;
- release of fission products to the coolant in case of clad rupture. Some important fission products are radio isotopes of iodine (^{131}I, ^{133}I, ^{135}I) and caesium (^{134}Cs, ^{136}Cs, ^{137}Cs);
- processes related to purposeful adding of impurities (oxygen for example) to the coolant.

In this chapter, we only look at the impurities in the lead or LBE before use. The impurities generated during operation are considered in Chapter 4 together with the methods for control and removal of them.

At the moment, no nuclear specifications exist for lead or LBE. However, different commercial materials seem to have an appropriate purity for nuclear applications. Commercial grades of lead content up to 99.98 wt.% of the basic metal are available. Typical lead and LBE impurity contents are given as examples in Table 3.3.1. [Ivanov, 2003] recommends C00 or C0 purity for lead and the chemical composition of LBE used for MEGAPIE experiment is given in Table 3.3.2 [Safety, 2002].

Silver is the only noticeable impurity which may be relevant for activation. It is activated under the neutron flux through the following reaction:

$$^{109}\text{Ag}\ (n,\gamma)\ ^{110m}\text{Ag},\ 250\ \text{d}$$

In addition to metallic impurities, there are some amounts of oxygen, nitrogen and hydrogen in the initial lead or LBE resulting from the conditions of cooling down of commercial material, overall dimensions of ingots and conditions of its further storage. Of concern is not only oxygen distributed in the volume of ingots but also oxygen in the near-surface layer of ingots as lead oxide (PbO). As a result of long storage of unprotected ingots in humid atmosphere, adsorbed moisture is transformed on their surface to the lead hydroxide in the reaction:

$$PbO + H_2O = Pb(OH)_2$$

Table 3.3.1. Chemical composition of commercial lead, wt.%

Elements	Lead brand			Elements	Lead brand		
	C00	C0	C1		C00	C0	C1
Ag	0.00001	0.0004	0.001	Tl	0.0001	–	–
Cu	0.00001	0.0005	0.001	Ca	0.0001	–	–
Zn	0.0001	0.001	0.001	Na	0.0001	–	–
Bi	0.0005	0.004	0.006	Cd	0.00005	–	–
As	0.0001	0.0005	0.001	Al	0.00005	–	–
Sn	0.0001	0.0005	0.001	Hg	0.00005	–	–
Sb	0.0001	0.0005	0.001	In	0.00001	–	–
Mg	0.0001	–	–	Mg+Ca+Na		0.002	0.003
Fe	0.0001	0.001	0.001	**Pb**	**99.99852**	**99.992**	**99.985**

Table 3.3.2. Metallic impurities in the LBE for MEGAPIE experiment [Safety, 2002]

Element	Content (μg/g)
Ag	25.6
Cd	2.2
Cr	0.19
Cu	26.5
Fe	1.4
In	14.4
Ni	2
Sn	5.9

3.4 Solubility data of metallic and non-metallic impurities in LBE and Pb

3.4.1 Solubility data of some metallic elements in pure Pb and liquid eutectic Pb-Bi

The procedures used for the determination of the solubility in the liquid metals cause some problems because subsequent chemical reaction or exchange of impurities (oxygen, nitrogen, carbon,...) between the liquid metal and the solid metal or compound may occur.

Generally, when the experimental technique is described, the solubility of a metallic element X in the considered liquid metals is obtained by putting the metal X (as a specimen or the crucible containing the melt) in contact with the liquid for several hours. Then a filtered few grams of this latter are sampled at the temperature of the test. The samples are then analysed. They are dissolved in a nitric acid solution and the X element content is measured by atomic absorption or by colorimetric techniques using some ortho-phenantroline for iron. When a constant X content is obtained, it is considered that the solubility value is reached and is taken equal to the constant value.

For a metallic element with a large solubility, a specimen is immersed in a liquid bath and the weight loss of the metallic specimen is regularly measured. When it is constant, then it is considered that the solubility of X element is reached. It is equal to the weight loss of the metallic specimen divided by the liquid bath volume.

A large amount of solubility data has been reported in [Tecdoc, 2002] (which is a compilation of data available in [Kozlov, 1983] and [Arnoldov, 1998]). The values of metallic solubility in LBE

mentioned by [Li, 2002] coming from [Gromov, 1997] [Orlov, 1997], [Adamov, 1998] are in agreement with those data. Table 3.4.1 gives the values of A, B of the equation used to characterise the solubility values as a function of temperature and the temperature range when it is specified.

$$\log S\ (\text{wt.\%}) = A - B/T \quad T(K)$$

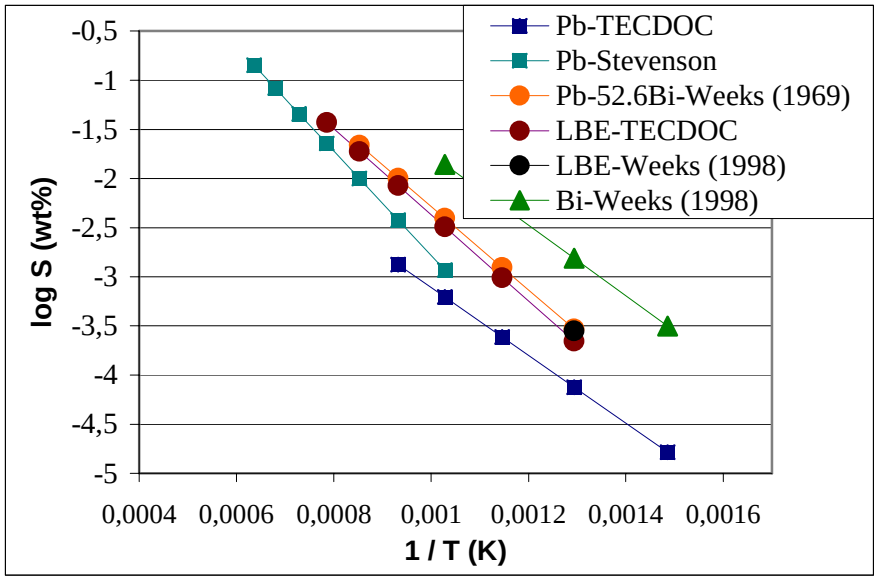
Table 3.4.1. Solubility of some elements in liquid Pb, and Pb-Bi

		Pb			***LBE***			
Element	**Ref.**	**T (°C)**	**A**	**B**	**Ref.**	**T (°C)**	**A**	**B**
Ni	[Tecdoc, 2002]	330-1300	2.78	1000	[Tecdoc, 2002], [Rosenblatt, 1969]	450-550	1.7	1000
Ni	[Alden, 1958]	340-800	1.3	1383	[Martinov, 1998]	400-900	1.53	843
Mn	[Tecdoc, 2002]	327-1200	2.02	1825				
Mn	[Pelzel, 1956]	474-1000	3.0445	3272				
Mn	[Elliot, 1965]	350-800	6.32	2690				
Co	[Tecdoc, 2002]	350-1650	2.60	4400	[Rosenblatt, 1969]	400-550	1.3	2834
Cu	[Tecdoc, 2002]	327-1000	2.72	2360	[Rosenblatt, 1969]	400-550	2.41	1920
Fe	[Tecdoc, 2002]	330-910	0.34	3450	[Tecdoc, 2002], [Martinov, 1998]	550-780	2.01	4380
Fe	[Weeks, 1969]	400-600 600-750	0.34 1.824	3450 4860	[Weeks, 1969]	500	Log (S) = -3.55	
		400-850	Log s = 5.051-1728/T + 3.633 $10^6/T^2$					
Fe	[Stevenson, 1961]	750-1300	2.53	5314	[Weeks, 1969]	525-840	1.96	4246
α Fe	[Ali-Khan, 1982]	1000-1650	3.67	2450				
α Fe	[Stevenson, 1961]		2.96	6100				
γ Fe	[Ali-Khan, 1982]	1000-1650	7.66	7100				
γ Fe	[Stevenson, 1961]		1.83	4800				
Cr	[Venkatraman, 1988]	808-1210	3.70	6720	[Courouau, 2004]	370-540	1.07	3022
Cr	[Tecdoc, 2002] [Alden, 1958]	908-1210	3.74	6750	[Tecdoc, 2002], [Rosenblatt, 1969]	400-500	-0.02	2280
Cr	[Venkatraman, 1988]		3.7	6720				
Mo	[Tecdoc, 2002]	1000	$<10^{-3}$ wt.%					
Mo	[May, 1982]	600-700°C	$<10^{-6}$ wt.%					
Mo	Shunk (1969)	800-1200	1.6	6000				
Mo	Brewer (1980)		2.92	10553.5				
W	Shunk (1969)	1200-1740	6.55	7150				
Si	[Tecdoc, 2002]	1050-1250	3.886	7180				
Zr	[Tecdoc, 2002]	500	~1.2 10^{-9} wt.%		[Tecdoc, 2002], [Weeks, 1969]	227-725	0.15	3172
Nb	[Tecdoc, 2002]	1000	$< 10^{-5}$ wt.%					
Ti	[Tecdoc, 2002]	500	~5.6 10^{-4} wt.%					
U	[Tecdoc, 2002]	400-800	3.921	5121				
C	[Tecdoc, 2002]	1170-1555	1.026	3850	[Tecdoc, 2002]		-1.36	1870

N_2 is not soluble in lead or LBE.

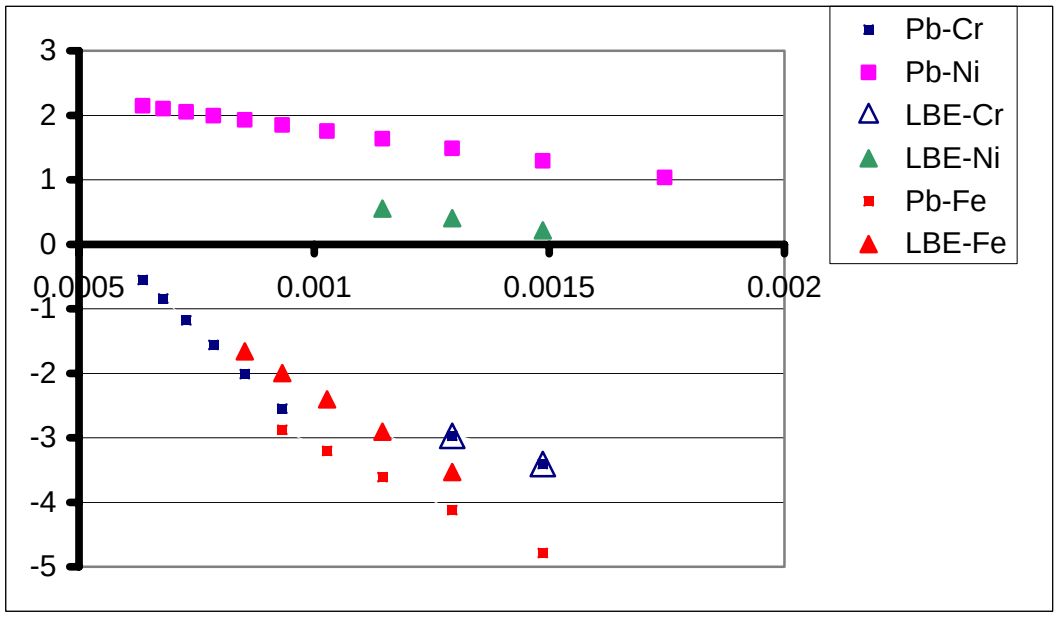
In Figures 3.4.1 and 3.4.2 the different solubility data for iron in, Pb, Bi and LBE are compared. The iron solubility is higher in liquid Bi than in liquid Pb. It is intermediate in LBE.

Figure 3.4.1. Solubility data of iron in liquid Pb, Bi and LBE



A comparison of the solubility of some metallic elements of interest from a corrosion point of view shows that, as has been reported by [Borgstedt, 1992], these data follow the general trends in the solubility of transition metals reported by [Guminski, 1990]: Ni and Mn dissolve to a large extent in low melting point metals while molybdenum has a very low solubility.

Figure 3.4.2. Solubility data of Fe, Cr, Ni in liquid Pb and LBE from [Tecdoc, 2002]



3.4.2 Solubility data of oxygen in pure Pb and LBE

Different determinations of the oxygen solubility limit in Pb and Pb-Bi have been performed. At the lowest temperatures (~500°C), sampling methods are generally used. At higher temperature, experimental techniques rest on rare earth stabilised zirconia probes. These probes allow not only the measurement but also the control of dissolved oxygen in Pb-Bi.

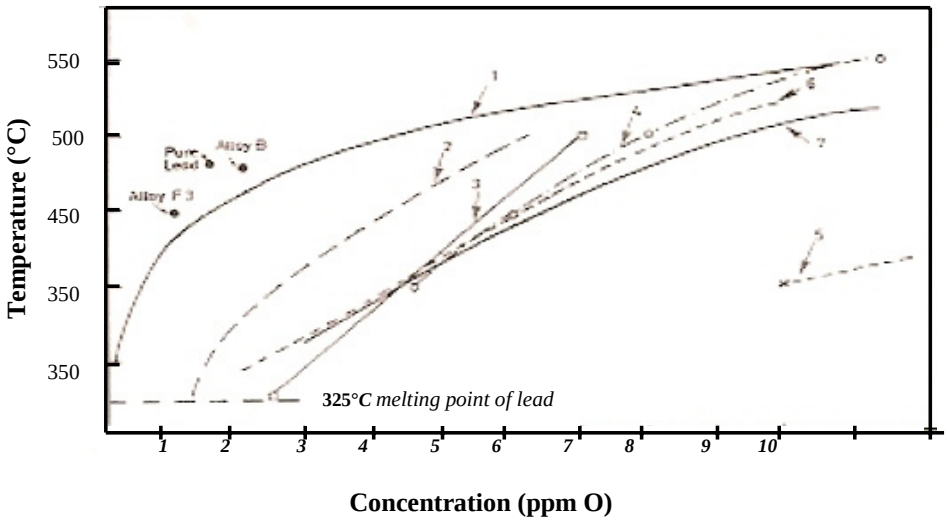
Different techniques have been used to determine the solubility limit of oxygen in Pb-Bi. Among these are the following:

1) After oxygen has been inserted in the liquid Pb bath, the bath is sampled. The Pb sample is melted again in a graphite crucible. The CO_2 production is then measured and converted to an oxygen concentration in the bath [Steen, 1982].
2) The oxygen content is obtained from calorimetric measurements [Rodigina, 1961].
3) Solid PbO is dissolved in the liquid and the oxygen content dissolved in the liquid is continuously measured by means of a rare earth stabilised zirconia probe [Taskinen, 1979].
4) Oxygen is introduced into the liquid by electrochemical techniques using a rare earth stabilised zirconia probe. The dissolved oxygen content is followed in parallel with a rare earth stabilised zirconia probe [Ghetta, 2002].
5) The oxygen solubility limit in LBE is deduced from the oxygen solubility limits in pure liquids Pb and Bi by thermodynamical calculations using free enthalpies of PbO and Bi_2O_3 oxides [Müller, 2003].

In a bibliographic review on the compatibility of structural steels with liquid lead, [Flament, 1988] reported on a study from [Steen, 1982] which compared the data obtained at temperatures lower than 550°C from various authors. These data are shown in Figure 3.4.3. [Steen, 1982] observed large discrepancies between them and concluded that the discrepancies probably are the consequence of the presence of stray oxide particles in the liquid lead and that in the 400-500°C temperature range, the oxygen solubility is low. From his work, he suggested a value of about 1 ppm.

Figure 3.4.3. Data of oxygen solubility in lead reported in [Steen, 1982]

1 – Reinert, 2 – Worner, 3 – Baker, 4 – Hansen, 5 – Bartfeld, 6 – Zausznica, 7 – Carlsson



Very recently, [Ganesan, 2006] reviewed some literature data on oxygen solubility in liquid Pb and LBE and presented new results. Based on the uncertainties on the data obtained from sampling methods [Risold, 1998], [Ganesan, 2006] considers only the data obtained mostly at high temperature by electrochemical methods.

Selected oxygen solubility data are reported in Table 3.4.2. The *A* and *B* parameters refer to the following equation:

$$\log (S \text{ wt.\%}) = A - B/T$$

Table 3.4.2. Oxygen solubility data in liquids Pb and LBE

Pb				*LBE*			
Ref.	**T (°C)**	**A**	**B**	**Ref.**	**T (°C)**	**A**	**B**
[Richardson, 1954]	940-1240	3.2	5050	[Gromov, 1998] [Martinov]	400-700	1.2	3400
[Rodigina, 1961]	300-400	3.1	4900	[Ghetta, 2004]	300-500	3.27	4852
[Heinzel, 2002]		1.64	3603	[Müller, 2003]	200-600	2.52	4803
[Alcock, 1964]	510-700	3.42±0.14	5240±120	[Courouau, 2004]	350-500	3.34	4962
[Swarc, 1972]	897-1080	2.76	5600	[Ganesan, 2006]	540-740	2.42	4287
[Charlé, 1976]	900-1100	3.2	5055				
[Isecke, 1977]	900-1100	3.38	5182				
[Taskinen, 1979]	800-845	3.38	5170				
[Conochie, 1981]	455-606	0.96	3007				
[Gromov, 1999]	400-700	3.2	5000				
[Ganesan, 2006]	540-740	3.21	5100				

Figure 3.4.4 represents the high temperature experimental data on oxygen solubility in liquid lead obtained by electrochemical techniques. From this figure, it appears that the data of [Szwarc, 1972] deviate from the others. [Ganesan, 2006] explains that the use of chromel wire as electrical lead would have contributed to this deviation due to the interaction of dissolved Cr and Ni with oxygen in molten Pb. The other data are in agreement, except those of (Conochie, 1981] at low temperatures.

Figure 3.4.4. Data of oxygen solubility in molten lead from Table 3.4.2

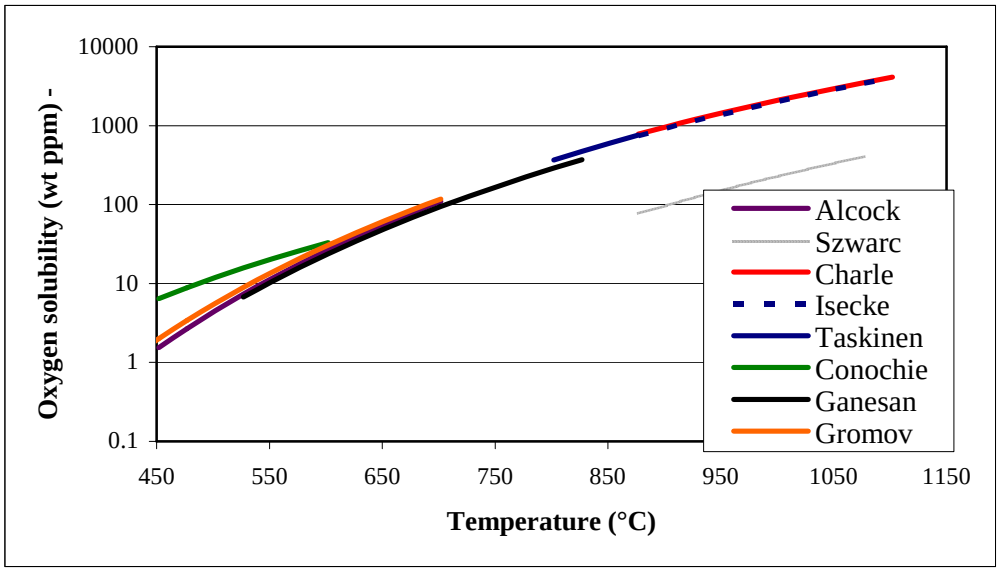
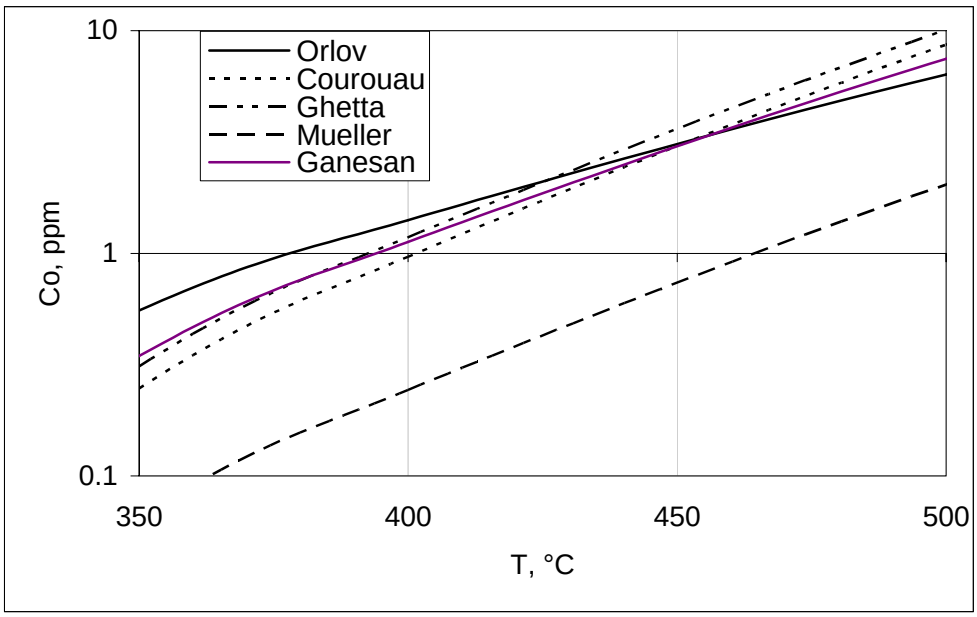


Figure 3.4.5 compares the values of oxygen solubility in molten LBE reported in Table 3.4.2. Except the estimation of [Müller, 2003] from the corresponding binary data, there is a good agreement between the different data.

Figure 3.4.5. Data of oxygen solubility in molten LBE



The more generally used values for oxygen solubility are:

$$\text{In lead: } \log S\ (\text{wt.\%}) = 3.2 - 5000/T(K)$$

$$\text{In LBE: } \log S\ (\text{wt.\%}) = 1.2 - 3400/T(K)$$

3.5 Diffusivity

3.5.1 Diffusivity data of some metallic elements

The diffusion coefficient of a solute in a melt is a fundamental quantity required to characterise mass-transport rates. However, there are numerous difficulties in accurately measuring diffusion coefficients in liquid metals, the main being the problem of mass transport by bulk motion of the fluid due to natural convection. This is driven by buoyancy forces produced by any temperature or concentration gradients which lead to decrease of liquid density with depth. Several different techniques exist to determine the diffusion coefficient in molten metals and generally their accuracy is of the order several %. A survey of these techniques is available in [Kubicek, 1983], [Shimoji, 1986].

Experimental techniques

Capillary techniques

Many diffusion coefficients in molten metals have been determined by means of capillary techniques. These techniques include:

1) *Capillary reservoir methods (with finite or semi-infinite capillary tubes)*. In this technique a long capillary tube containing the pure molten metal is immersed in a large reservoir of the same molten metal containing a known concentration of the metal whose diffusion rate is desired to be measured. Concentration of the diffusing species is successfully determined by using radionuclides or X-ray spectral analysis.

   Some specific arrangements have been developed to improve these methods. For example, it has been developed a shearing cell consisting in six discs that can rotate around an axial pin. The capillaries in three of the discs are filled with pure melt and a fourth is filled with melt containing a radioactive diffusing species. The outmost disc serves to close off the capillaries. As soon as the capillaries are aligned, diffusion starts. After a certain period, the discs are revolved to shear the column into four segments. Sometimes, the capillary reservoir method has been combined with use of high temperature galvanic cell in particular to determine the oxygen diffusion coefficients in various liquid metals. The main advantage of this method is that the diffusion coefficient is measured in situ, not by subsequent analysis.

2) *Stationary diffusion source methods*. With this method the species whose diffusion is to be investigated is allowed to come into contact with the liquid through a gaseous phase. This method avoids some of the shortcoming of the capillary reservoir technique and is efficient with radionuclides.

3) *Reactive diffusion methods*. With this method the solid phase is allowed to come into contact with the melt.

The above methods suffer from several shortcomings including convection (during immersion of the tube or due to difference of density, mechanical effects, thermal gradient), inaccurate initial or boundary conditions, surface diffusion, inaccuracy in determining the concentration profiles of the diffusing species or phenomena arising during solidification.

Controlled forced convection techniques

The errors due to convection can be suppressed by imposing controlled force convection. When the dissolution of a solid in a liquid is diffusion controlled in the liquid boundary layer, the method of rotating disc dissolution can be used. This method uses a rotating disc which dissolves in a static melt. The rate of rotation is chosen so that laminar flow is achieved. The weight loss of the disc combined with the time of dissolution and angular velocity allow determination of the diffusion coefficient. The control of convection can also be insured by applying electromagnetic stirring.

Electrochemical methods

Electrochemical techniques are especially suitable for the determination of diffusion coefficients in the melt because convection is suppressed or eliminated. The experiments last only few seconds in contrast to the capillary methods and the wall effects are not encountered. Of these methods, the most important in the study of diffusion in melts are chronopotentiometry and rotating disc electrode (RDE). Linear voltammetry and polarography have limited application.

In the chronopotentiometry method, a pulse of current density is used to disturb the system from its equilibrium and the potential variation with time of the investigated electrode is measured. In the rotating disc method, an increasing voltage is applied to the RDE and the current is measured. In the linear voltammetry method, an increasing potential is applied to the working electrode. The current intensity variations with time and its maximum are measured.

Available data

Only a few data for diffusion coefficients of metallic elements in liquid lead and lead bismuth are available in the literature. Special attention is paid to the iron coefficient because iron diffusion in liquid lead alloys is the limiting step of the corrosion of iron and iron chromium alloys such as T91 (Fe-9Cr).

The iron diffusion coefficient in Pb-Bi, is known at only three temperatures:

- 400°C: 3.5×10^{-7} cm^2/s [Balbaud 2004];
- 470°C: 7.6×10^{-6} cm^2/s [Balbaud, 2004];
- 750°C: 2.27×10^{-5} cm^2/s [Benerjee, 1974].

These data have been obtained by means of experiments with a rotating disk specimen [Benerjee, 1974] or a T91 steel (Fe-9Cr) cylinder [Balbaud, 2004]. The specimen dissolution rate is limited by iron diffusion in the boundary layer and is determined by a weight loss measurement. It depends on the temperature, time, rotating speed, liquid viscosity, the solubility and diffusivity of the solute.

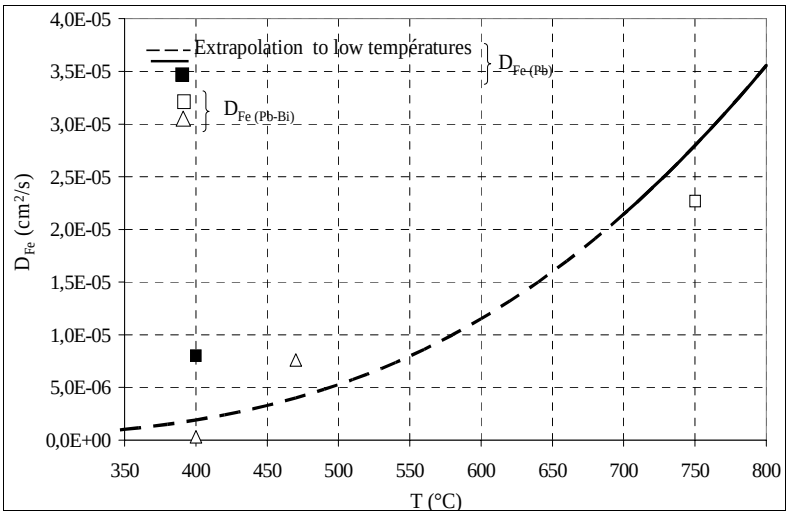
The iron diffusion coefficient in lead has been determined by analysing the grooving of grain boundaries by the liquid metal [Robertson, 1968]. With this method the liquid metal in contact with the solid dissolves the grain boundaries to form grooves. The groove width is linked to the diffusion coefficient of solid elements in the liquid.

Figure 3.5.1 shows that the diffusion coefficients for iron in liquid Pb and LBE are not very different. The data determined at low temperature are not far from the extrapolated values for iron from high temperatures (700°C-1000°C) [Robertson, 1968].

The iron diffusion coefficient in LBE is approximated to that in lead and they correspond to the extrapolated values of [Robertson, 1968]:

$$\mathrm{Log}\left(D\ \mathrm{cm}^2/s\right) = -2.31 - \frac{2295}{T}\ (700°\mathrm{C} < T < 1000°\mathrm{C})$$

Figure 3.5.1. Iron diffusion coefficient in pure Pb and eutectic Pb-Bi



Selected diffusion coefficient data for different metallic elements in lead are also reported in the literature and given in Table 3.5.1.

Table 3.5.1. Diffusion coefficients of some metallic elements in lead liquid

Element	Temperature range (°C)	Diffusion coefficient ($cm^2\ s^{-1}$); R ($J\ mol^{-1}\ K^{-1}$)	Reference
Co	750-1000	$4.6\ 10^{-4}\ \exp(-22154/RT)$	[Robertson, 1968]
Se	550-900	$3.4\ 10^{-4}\ \exp(-12958/RT)$	[Lozovoy, 1981]
In	450-900	$3.1\ 10^{-4}\ \exp(-13794/RT)$	[Lozovoy, 1981]
Tl	450-900	$3.1\ 10^{-4}\ \exp(-15884/RT)$	[Lozovoy, 1981]

3.5.2 Oxygen diffusion coefficient

Different techniques have been used to determine the oxygen diffusion coefficient.

1) Electrochemical measurement with a rare earth stabilised zirconia electrode [Szarc, 1972], [Bandyopadhyay, 1971], [Honma, 1971]: the principle is to perform amperometries at the oxygen reduction potential. The variations of the current intensity are related to the diffusion coefficient of oxygen in the lead.
2) Electrochemical measurements with a rare earth stabilised zirconia electrode on each side of a horizontal column of liquid lead. One probe is used to introduce oxygen into the liquid. The other, on the opposite side of the lead column is used to measure oxygen concentration as a function of time via its potential. This data is then to determine the oxygen coefficient diffusion coefficient.
3) Measurement of the weight loss of a PbO rotating disc [Gromov, 1996]. The dissolution kinetics of PbO in liquid lead or LBE depends on the oxygen solubility, the rotation speed of the disc, the viscosity of the liquid and the diffusion coefficient of oxygen at the temperature.

Selected oxygen diffusion coefficient data are given in Table 3.5.2 and Figure 3.5.2.

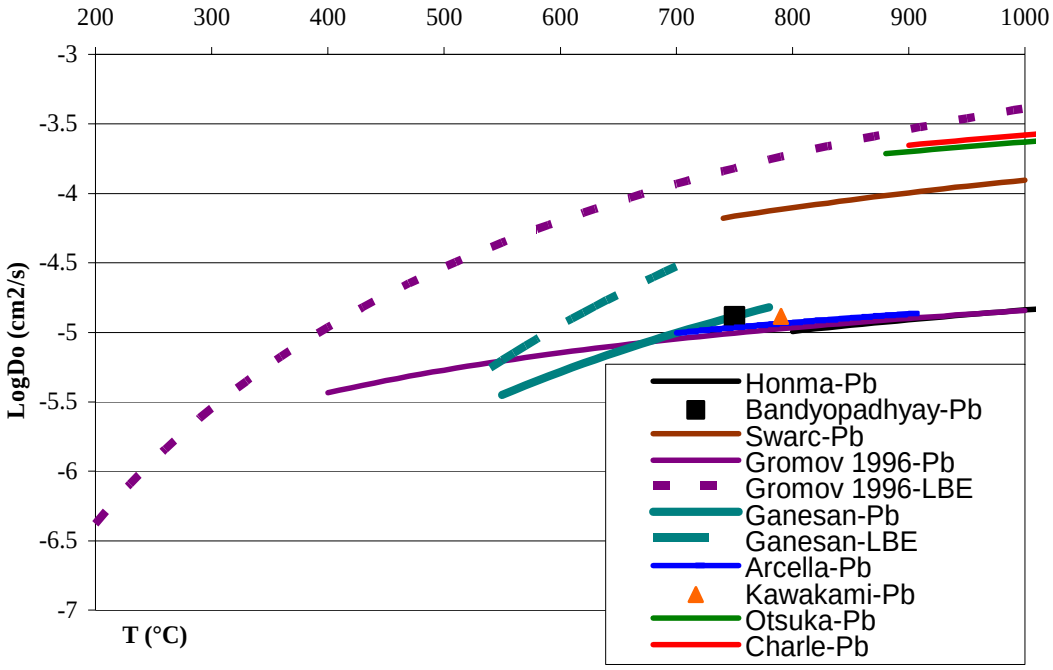
Table 3.5.2. Data on oxygen diffusion coefficient in liquid lead and LBE

Liquid	Temperature range (°C)	Diffusion coefficient of oxygen ($cm^2\ s^{-1}$), R($J\ mol^{-1}\ K^{-1}$)	Reference
Pb	700-900	$6.32\ 10^{-5}\ \exp(14979/RT)$	
Pb	800-1100	$(9.65 \pm 0.71)10^{-5}\ \exp\ (-20083 \pm 6067/RT)$	[Homna, 1971]
Pb	750	$1.29\ 10^{-5}$	[Bandyopadhyay, 1971]
Pb	740-1080	$(1.44 \pm 0.45)10^{-3}\ \exp(-25942 \pm 2803/RT)$	[Swzarc, 1972]
Pb	900-1100	$(1.48 \pm 0.6)\ 10^{-3}\ \exp(-19497 \pm 10711/RT)$	[Otsuka, 1975]
Pb	900-1100	1.90 10-3 $\exp(-20920/RT)$	[Charle, 1976]
Pb	400-1000	$6.6\ 10^{-5}\ \exp(-16158/RT)$	[Gromov, 1996]
Pb-Bi	200-1000	$2.39\ 10^{-2}\ \exp(-43073/RT)$	[Gromov, 1996]

The following observations are made:

1) The differences between the data in lead may result from the differences between materials used for the rare earth stabilised zirconia probe.
2) The results obtained with the rare earth stabilised zirconia probe are not very different from those obtained with a rotation disc.
3) There is a significant scatter of the different values except in the 600-700°C temperature range.
4) The oxygen diffusion coefficients in lead and LBE differ by two orders of magnitude.

Figure 3.5.2. Oxygen diffusion coefficient in liquid lead and lead-bismuth



3.6 Chemical interactions and ternary phase diagrams

During operation, lot of spallation products will be generated in the LBE target. In particular mercury is expected to be the most generated species. Therefore, the ternary Pb-Bi-Hg system has been investigated [Maître, 2002]. Phase limits and invariant equilibria were determined by differential Scanning Calorimetry (DSC). The phase diagram computation was performed using Calphad method [Kaufman, 1970] with Thermocal software.

Two isothermal sections at 310 K and 355 K of the ternary phase diagram are given in Figures 3.6.1 and 3.6.2.

The 310 K section emphasises a peritectic equilibrium:

$$C = Liq + Fcc\ (Pb) + Rhombo\_A7(Bi)$$

where C is $Bi_{0.35}\ Hg_{0.20}\ Pb_{0.45}$.

The 355 K section shows another invariant:

$$Liq + hcp\_\varepsilon(Bi,Pb) = Fcc(Pb) + Rhombo\_A7(Bi)$$

The isopleth section X_{Pb}/X_{Bi} = O.45/0.55 (Figure 3.6.3) shows the decrease in liquidus and solidus temperature as the Hg content increases.

Figure 3.6.1. Isothermal section at 310 K for the ternary Pb-Bi-Hg system [Maître, 2002]

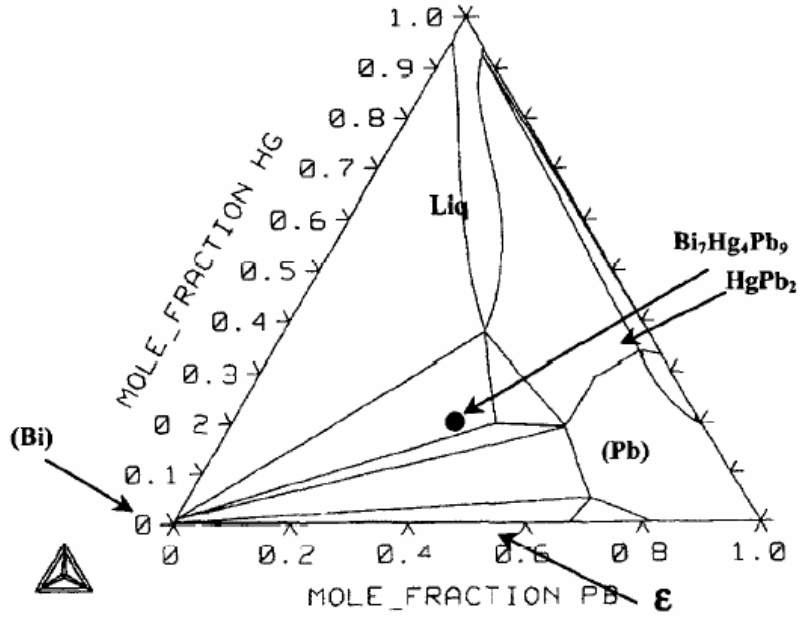


Figure 3.6.2. Isothermal section at 355 K for the ternary Pb-Bi-Hg system [Maître, 2002]

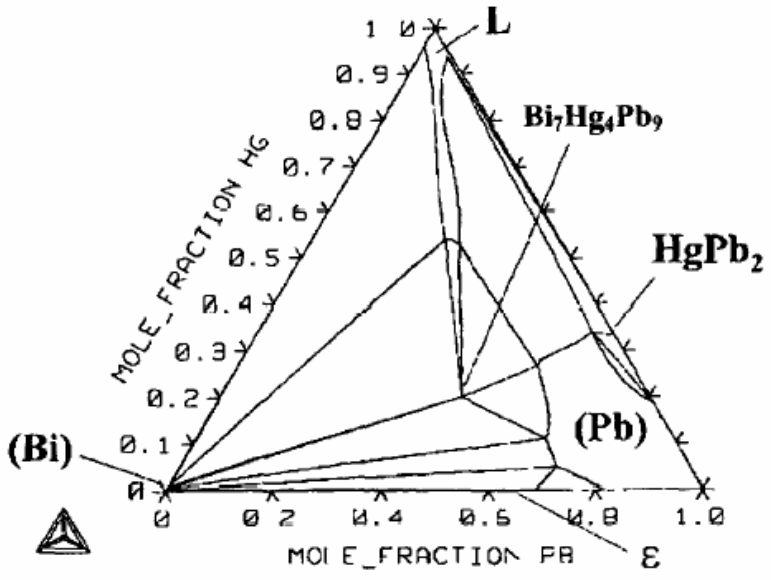
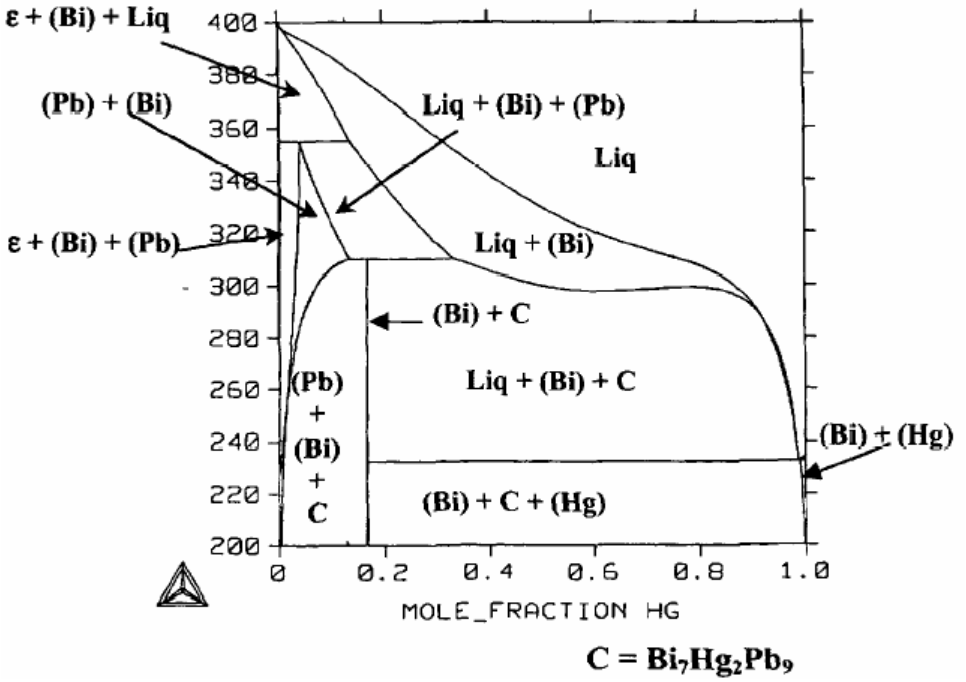


Figure 3.6.3. Isopleth section (X_{Pb}/X_{Bi} = O.45/0.55) in Pb-Bi-Hg. Temperature is given in K [Maître, 2002].



3.7 Lead and LBE-water interaction

The increasing interest in heavy liquid metal reactors, based on either lead or lead-bismuth eutectic coolants, raises the question of the effects of their possible interaction with water. The preliminary designs of lead fast reactor (LFR) and of subcritical transmutation systems prototypes, presently foresee the use of steam generation modules in direct contact with the liquid metal of the main vessel. With this configuration an accidental leakage of water into the core vessel cannot be excluded. Moreover, an incidental scenario which could cause a physical interaction between LBE and heavy water has been considered and studied for the MEGAPIE experiment [MSR, Jacobs]. The consequences of such an event must be thoroughly examined due to its impact on the design, the maintenance and the economics of these future reactors.

It should be pointed out that, unlike the cases of sodium or lithium and its alloys, for Pb and PbBi there is no chemical interaction with water and the resulting effects are significantly different.

3.7.1 Literature survey

From a literature review, three main categories of experiments were found:

1) Pb-17Li large-scale experiments [Kottowski, 1991], [Ciampichetti 1, 2003a], [Ciampichetti 2, 2003b];
2) small-scale experiments involving Pb, Pb-17Li, 2Pb7Li and Li [Kranert, 1991];
3) small-scale Pb-Bi experiments [Sibamoto, 2001], [Corradini, 1988], [Nakamura, 1999], [Hibiki, 2000], [Suzuki, 2003].

Large-scale experiments

Large-scale experiments were mainly performed in Ispra and Brasimone with Pb-17Li for fusion applications. Their characteristics are given in Table 3.7.1.

Table 3.7.1. Large-scale experiments

Water pressure	Water temperature	Injected mass of water	Liquid metal temperature	Volume of the reaction vessel
40 to 155 bar	225 to 325°C	2.7 to 4.6 kg	350 to 500°C	50 to 100 litres

Due to the chemical and physical interactions, strong and rapid pressure and temperature rises were observed. In some tests, some spikes were detected above the water injection pressure.

LIFUS 5 and BLAST experiments ([Kottowski, 1991], [Ciampichetti 1, 2003a], [Ciampichetti 2, 2003b]) dealt with the interaction between Pb17Li alloy and hot pressurised water coming from large leaks, simulating a cooling tube rupture inside the water-cooled liquid lead-lithium (WCLL) blanket. Due to the production of hydrogen in these experiments, it is not possible to extend the results to the accident scenarios foreseen in lead reactors.

Small-scale experiments

Small-scale experiments made by JRC Ispra [Kranert, 1991], consisted of the injection of water from the top of an expansion tube (d = 9 mm, L = 2 m) into a reaction capsule containing the alloy (d = 24 mm, L = 170 mm) without cover gas buffer. The test conditions are given in Table 3.7.2.

Table 3.7.2. Conditions of small-scale experiments [Kranert, 1991]

Water pressure	Water subcooling temperature	Injected mass of water	Liquid metal temperature
1 to 25 bar	10 – 43 – 75°C	1.2 to 200 g	500 to 800°C

The results of the tests carried out with lead and a water injection pressure of 1 bar showed a pressure rise of up to 18 bar due to the coolant column impact on the alloy surface. The 18 bar pressure rise is the highest observed value, excluding the tests with lithium. In fact, an important conclusion of this work was that the chemical reaction between the alloys containing lithium and water inhibits a violent thermo-hydraulic reaction due to the attenuating effect of the hydrogen produced.

A small-scale LBE experiment was performed at JAERI in the frame of reactor safety. The liquid metal was dropped into a water pool having the features shown in Table 3.7.3 [Sibamoto, 2001], [Nakamura, 1999].

Table 3.7.3. Conditions of the JAERI small-scale experiment

Water pressure	Water temperature	Liquid metal temperature	Mass of water	Mass of LBE
1 bar	100°C	250°C	80 g	1.8 kg

These experiments demonstrated that the melt accumulation in the water pool is accompanied by vigorous steam generation at the initial point of contact of the PbBi with water. A violent vapour expansion occurred and was well predicted by a simplified one-dimensional model. The evolution of steam production and expansion was measured by a neutron radiography technique.

For the development and validation of the SIMMER code, [Hibiki, 2000] and [Suzuki, 2003] reported some experimental studies on flow characteristics in gas-molten metal pool. [Corradini, 1988] presents some criteria to predict the conditions for a vapour explosion.

3.7.2 Related risks

The main risk for the structures is associated with the occurrence of a vapour explosion. A vapour explosion is a physical event in which a hot liquid rapidly fragments and transfers its internal energy to a colder, more volatile liquid which in turn vaporises at high pressure and expands, doing work on its surroundings. The vapour explosion criterion advanced by Fauske is based on the comparison between interface temperature and the spontaneous nucleation temperature. For fluids hardly wetting, like water and LBE, the spontaneous nucleation temperature is very close to the homogeneous nucleation temperature which is approximately 310°C for water. This criterion, even if not universally accepted, was confirmed by recent observations collected by [Kurata, 2004] which show that, at 1 atmosphere pressure, a steam explosion is possible over an interface temperature range from about 300°C to the water critical temperature. Other observations by [Kurata, 2004] include:

- Vapour explosion can occur at initial melt temperatures and between about 400°C and 500°C at pressures under 0.1 MPa.
- Vapour explosions seem to occur when the water is sufficiently subcooled, and when the contact temperature is higher than the spontaneous bubble-nucleation temperature.
- Vapour explosions do not occur at pressures above 0.2 MPa.
- Decreasing droplet subcooling diminishes the explosion intensity.

In case where vapour explosions do not occur, the expansion of released water in LBE happens at a slower rate and simpler thermodynamic models can describe the behaviour.

In any case it is advisable that liquid metal/water interaction be studied by means of both experimental and numerical approaches.

3.7.3 Numerical codes

In view of the safety issues related to the severe core melting accident, several numerical codes have been developed in the recent years to assess the effects of the interaction between liquid metals and water. Among these are:

- Mattina;
- SIMMER.

Mattina [Jacobs, 2002] was recently used to simulate a case of LBE-water interaction for the MEGAPIE project. Its limitations are that the code is not suitable for the treatment of film boiling conditions and that the equations of state for lead and lead-bismuth were not originally implemented.

SIMMER is a complex fluid-dynamic code coupled with a neutron kinetics model that has been used to model liquid metal/water interactions [Corradini, 1998], [Hibiki, 2000], [Suzuki, 2003]. The fluid dynamic part is suitable for the modelling of liquid metal/coolant interactions having several different patterns and its data base includes the physical properties of lead and LBE as well.

3.8 Lead or LBE and sodium interaction

There are a number of applications where lead or LBE are used in the same system as sodium. In these cases it is possible for lead or LBE to contact sodium. Such applications include:

- accelerator-driven technology for waste transmutation systems where LBE is used for the spallation target and sodium is used for the transmuter blanket;
- in advanced intermediate heat exchangers (AIHX) for fast breeder reactors in which the secondary liquid sodium is replaced by LBE;
- when a sodium-bonded metallic fuel is deployed inside a LBE cooled blanket.

In all the cases, the consequences of contact between the different liquids under accident conditions have to be considered and evaluated. The information given hereafter is taken from [Crawford, 2001].

Figures 3.8.1 and 3.8.2 show the binary phase diagrams for the Na-Pb and Na-Bi systems respectively [Borgstedt, 1996]. While a ternary Na-Pb-Bi diagram would be more appropriate, the binaries allow an estimate of the potential stable phases for LBE/Na interaction.

These phase diagrams show that Bi is less soluble in Na than Pb but Bi is not insoluble as can be seen from the equation reported by [Walker, 1970].

The Na-Pb compound melting temperatures are around 400°C or less while Na_3Bi melts at 840°C.

Moreover, from different studies conducted as part of various programmes, the known products that stemmed from the reaction between Na and Pb or Na and Bi are listed in Table 3.8.1 together with the identified enthalpies of formation. The negative values of the enthalpies of formation indicate that these compounds are stemmed from an exothermic reaction.

Figure 3.8.1. Na-Pb phase diagram from [Borgstedt, 1996]

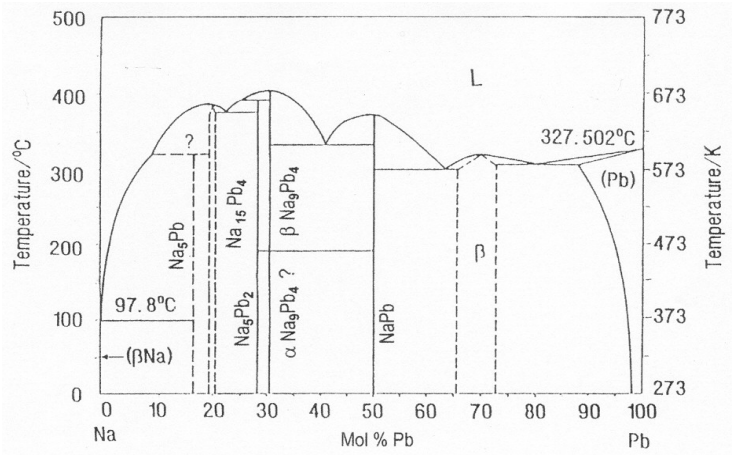


Figure 3.8.2. Na-Bi phase diagram from [Borgstedt, 1996]

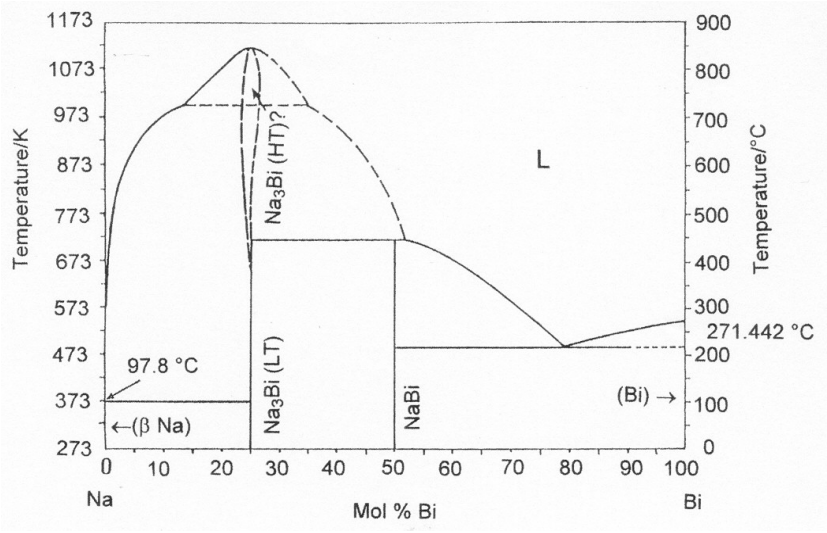


Table 3.8.1. Known reaction products from Na and Pb or Na and Bi reactions

Compounds	$\Delta H_f°$ (298), kcal/mole
Lead	
$Na_{15}Pb_4$	–
Na_5Pb_2	-35.0
Na_9Pb_4	–
NaPb	-11.6
$NaPb_3$	-15.2
Na_4Pb	-20.0
Bismuth	
Na_3Bi	-48.2
NaBi	-15.6

Experimental tests for phase identification consisted of placing measured quantities of Pb or Bi metal onto a measured quantity of solid Na in the bottom of a Petri dish. The metals were then heated in an argon atmosphere from 25°C to a temperature above the melting temperature of Na. Each experiment was terminated after the observed reaction was complete or after the metals had melted and mixed. It has been mentioned “no visible exothermic reaction was noticeable at the melting points of sodium or lead. Once the lead melted, it mixed well with the molten sodium.” [Crawford, 2001]. For the Na-Bi reaction, “A very vigorous exothermic reaction took place at the melting point of sodium. A grey-to-black friable material resulted from the exothermic reaction.” [Crawford, 2001]. The following general observations and/or accomplishments were made as a result of the experimental programme:

1) Investigations and calculations are performed to evaluate the temperature excursion when Na and Bi are put in contact.
2) The Na-Bi reaction is rapid and releases a relatively high amount of heat. The Na-Pb reaction seems less severe but the reason for that is not obvious based on the values of compound formation enthalpies.

3) In the case of a Na cooled transmuter blanket and a LBE target, in analysing the consequences of a blanket-target interface leak, some phenomena must be considered:

   a) The Na-Bi and Na-Pb reaction products might plug the leak, stopping the reaction and leading to a benign event.

   b) The Na-Bi and Na-Pb reaction products might form in the leak area and stress the target wall, exacerbating the failure and leading to more but this seems not very likely because the material inboard of the target wall would be liquid LBE and there would be nothing solid to maintain the reaction products in a position to stress the original leak area.

   c) The Na-Bi and Na-Pb reaction products could be swept away by the flowing Na coolant, where they might dissolve or might simply disperse as solids in the coolant. Looking at the Na-Bi and Na-Pb phase diagrams indicates that the Na-Pb intermetallic is unstable in dilute solutions of Pb in Na, but that the Na_3Bi intermetallic would be present in dilute solutions of Bi in Na up to temperatures near 600°C. Furthermore, the Na_3Bi reaction product would likely remain solid at coolant temperatures, whereas the $Na_{15}Pb_4$ reaction product, if at sufficiently high Pb content to remain stable, could precipitate out of Na solution at coolant inlet temperatures. Therefore, it is possible that some reaction products will remain solid in the Na coolant. These products could potentially block flow channels depending on their amount and on their degree of dispersion.

   d) If the supply of reacting Na and Bi is not mitigated, significant heat energy from the reaction might be deposited to the blanket or target components but the ability of Na and LBE to dissipate heat and the available volume of Na to absorb the heat would likely prevent such a development.

4) In conclusion, a reaction between sodium and bismuth appears to be sufficiently exothermic that local temperatures could increase substantially, either adversely affecting further reaction, or perhaps introducing reaction products that might block flow channels. Experiments and calculations to assess reaction kinetics and the phenomenology of the reaction in representative conditions of the considered system are needed to well estimate the consequences on the contact between Na and Bi and Pb.

Some experiments have also been conducted by [Saito, 2005] to investigate the reaction between LBE and sodium. They consist in introducing some small amounts of LBE as droplets into a sodium bath. The tests were performed at different temperatures of Na and LBE (between 573 and 673 K) and with various LBE amounts (40 to 140 g as 1-2 mm diameter droplet for 1100 g of Na). The following results were obtained:

- The sodium temperature immediately rises by dropping LBE into liquid sodium due to an exothermic reaction between Na and LBE.
- The reaction between Na and LBE occurs more quickly when the temperature of the melts is high.
- Fine reaction products are formed and they mainly consist in $BiNa_3$ intermetallic compound. Amount of LBE affects the amount of reaction products and reaction heat.
- The reaction heat deduced from the temperature increase is comparable to the calculated $BiNa_3$ standard enthalpy value.

3.9 LBE and Pb and organic compounds interaction

The MEGAPIE spallation neutron target uses Diphyl THT (DTHT) oil, produced by Bayer, to cool the LBE target. In the case of a heat exchanger leak, high pressure DTHT will enter the low pressure LBE. Therefore, the consequences of such an event, particularly from a safety point of view, must be evaluated by investigating the chemical and thermal interactions between DTHT and LBE. Therefore, a set of experiments was carried out and is reported in [Leung, 2003]. These experiments consisted of putting DTHT with and without LBE in an autoclave at 350°C under an argon atmosphere.

The results show that:

- No chemical reaction occurs between oil and LBE which induces an increase of temperature and pressure detrimental to MEGAPIE experiment.
- There is a significant difference between apparent gas production rates of the DTHT and DTHT-LBE mixture at elevated temperature. But the net gas production at room temperature was virtually the same in the two cases. This suggests the production of a condensable gas in the experiment with only DTHT.
- There is a lower pressure rise than that which would be expected from the supplier information.

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