A new method for determining oxygen solubility in molten carbonates and carbonate–chloride mixtures using the oxidation of UO_2 to uranate reaction

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Abstract

One of the possible pyrochemical reprocessing procedures for spent ceramic nuclear fuels may involve the oxidation of UO_2 in alkali metal carbonate and carbonate-based melts, and this is controlled by the level of dissolved oxygen in the melt. A quantitative relationship has been derived between the extent of UO_2 oxidation and the concentration of oxygen (peroxide/superoxide) species formed upon oxygen dissolution in carbonates. A novel sensitive method for determining oxygen solubility in molten carbonates and carbonate-based melts has thus been developed. The concentrations of the alkali metal uranates(VI) formed can then be accurately determined without interference from unreacted UO_2. Oxygen solubilities at temperatures from 450°C to 800°C have been determined. The solubility of oxygen in a range of carbonate–chloride melts was also determined and found to increase with decreasing radius of the cation of the alkali metal chloride added. Measurements at various partial pressures of oxygen allowed the determination of the predominant oxygen species formed in the melt, and preliminary experiments showed that in the ternary carbonate melt, at 450°C, oxygen dissolves forming mainly superoxide ions. The applicability of Henry's Law in this situation is examined. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

A few years ago a project was originated in the UK to study the possible application of alkali metal carbonate and carbonate-based melts for pyrochemical reprocessing of spent ceramic nuclear fuels. As a major part of that study, the behaviour of uranium dioxide in these media was investigated [1–4], with the aim of finding optimal conditions for converting uranium dioxide into more easily soluble uranium species. This process results in the formation of a variety of alkali metal uranates(VI) which are essentially insoluble in carbonate melts [5,6] and can be filtered out and then dissolved in a dilute mineral acid, yielding the corresponding uranyl species.

The reaction of uranium dioxide with melts of alkali metal carbonates under oxidising conditions were first investigated some ten years ago by Kryukova et al. [7]. They examined the kinetics of the oxidation of UO_2 in the ternary carbonate melt, $(Li–Na–K)_2CO_3$, between 410°C and 500°C and reported the formation of non-specified diuranates(VI). They also found that the yield of the diuranates increased upon increasing the partial pressure of oxygen above the melt.

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We have recently carried out an extensive study of the oxidation of UO_2 in various alkali metal carbonate melts between 450°C and 900°C under a variety of oxidising conditions [1–3]. Initial experiments showed that there was an unquestionable qualitative dependence of the extent of the oxidation reaction on the solubility of oxygen in the media [1]. When the yields of uranates(VI) achieved in stirred melts after 7 h were compared with the total oxygen solubility measured under similar conditions in the corresponding melts, a clear similarity in the behaviour of these two sets of data with temperature was observed [1]. Under static conditions the rate and extent of oxidation also depends on the rate of oxygen dissolution in the melt and the diffusion of the oxygen species towards the UO_2 particles. These species, formed in the melt–gas interface (where oxygen dissolution occurs), diffuse into the bulk of the molten salt. Stirring the melt or bubbling in air or oxygen can eliminate or minimise this problem of slow diffusion and also saturate the melt with oxygen species as well as maintaining their concentration. Thus, when unstirred melts containing unreacted UO_2 were oxygenated, more of the UO_2 was converted to uranate. The concentration of uranate(VI) species formed in such melts would increase but the reaction ceased after 2–4 h and no further oxidation occurred, even though bubbling was maintained, Fig. 1. This is because the reaction now depends on the rate of diffusion of oxidising species (peroxide and superoxide) present in the melt through a layer of uranates formed on the surface of UO_2 particles that in turn depends on the concentration of the oxygen species in the melt.

We further found that more UO_2 could be oxidised in the carbonate melts if alkali metal chlorides were added [2], and this was expected since it is known that oxygen solubility in carbonate–chloride melts is greater than in the corresponding pure carbonates under similar conditions [8]. In all the cases investigated, the oxidation resulted in the formation of a mixture of alkali metal mono- and diuranates, the composition of which depended on temperature and the cations present in melts [1,2]. We thus set out to establish if a quantitative relationship existed between oxygen solubility in molten carbonates, and carbonate-based melts, and the extent of UO_2 oxidation in these systems. This would enable one to predict the amount of UO_2 that can be oxidised in a given carbonate melt under specified conditions and therefore to assess the technological feasibility of a chosen system. Alternatively, the oxidation of UO_2 in carbonate and carbonate-based melts can be used to measure oxygen solubility in these media.

Oxygen dissolves in alkali metal carbonate melts essentially only chemically. The oxide ion is not formed and only peroxide, superoxide and, possibly, percarbonate species have been identified [7–13]:
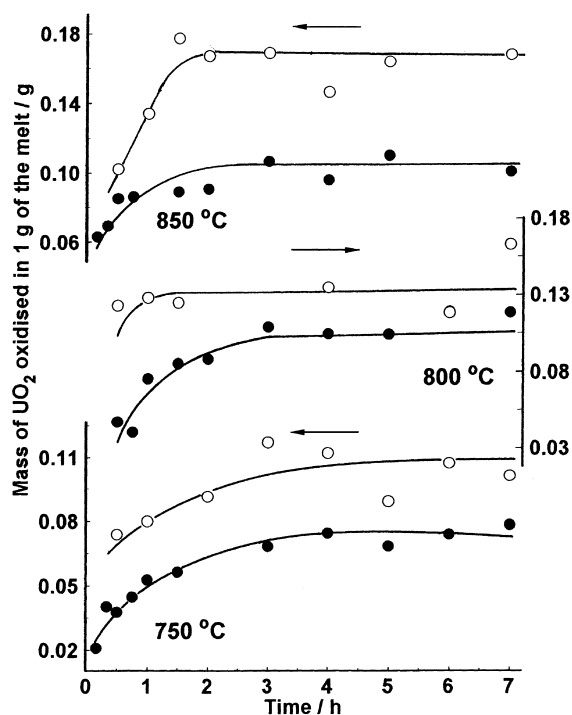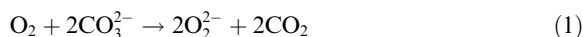

Fig. 1. Effect of stirring on the oxidation of UO_2 in $(Na–K)_2CO_3$ melt in air at A, 750°C; B, 800°C and C, 850°C. Results obtained under static conditions are shown by solid symbols and for stirred melts by empty symbols. Melt stirred by an eccentrically rotated alumina rod (100 rpm).

$$O_2 + 2CO_3^{2-} \rightarrow 2O_2^{2-} + 2CO_2 \qquad (1)$$

$$3O_2 + 2CO_3^{2-} \rightarrow 4O_2^{-} + 2CO_2 \qquad (2)$$

and possibly

$$O_2 + 2CO_3^{2-} \rightarrow 2CO_4^{2-}. \qquad (3)$$

The possible stabilisation of dissolved molecular oxygen has also been proposed [17] for $(Na–K)_2CO_3$ melt, but only in acidic melts under a high pressure of carbon dioxide.

Two general techniques can be employed for the determination of oxygen solubility in carbonate media. One is a so-called quenching method, used by Appleby and Van Druen [8] and by Nishina et al. [10]. Since the solubility of oxygen in molten carbonates increases with temperature increase, unlike in molecular liquids, the oxygen dissolved is released upon quenching the melt. A sample is withdrawn from a thermostatted melt saturated with oxygen; cooled in a closed chamber under an inert gas; and all gases evolved are collected and analysed. The second method involves saturating the melt with oxygen under the desired conditions and then titrating the melt with a suitable reducing agent: Schenke

et al. [11] have used Na_2SO_3 and Smith et al. [12] used $Cr_2(SO_4)_3$.

These techniques were usually employed with melts above 700°C, where the oxygen solubility was sufficiently high to allow its determination, but the results were subject to significant errors at lower temperatures. The scattering of data reported by Smith et al. [12] for the $(Li–K)_2CO_3$ eutectic melt, for example, was between 50% and 100%. Uranium dioxide can, in principle, also be used as a reducing agent. Its major advantage is that the concentration of uranium(VI) species formed can be determined accurately, even in the presence of a large excess of unreacted (unoxidised) UO_2. This is because a very sensitive method is used for determining the concentrations of U(VI) and, more importantly, there is no interference from the necessary excess of unreacted UO_2 present.

Although the formation of peroxide or superoxide species, upon dissolution of oxygen in molten carbonates, is now widely accepted, oxygen solubility is still often expressed in terms of the constant obtained using Henry's law, h_c, in mol dm^{-3} atm^{-1} (where 1 atm = 10^5 Pa). Henry's law assumes direct proportional dependence of the concentration of dissolved oxygen ([O]) on the oxygen partial pressure in the atmosphere above the melt (pO_2), viz.,

$$[O] = h_c pO_2. \tag{4}$$

This relationship holds for simple physical dissolution. In practice, the presence of peroxide, superoxide and percarbonate ions, reactions (1)–(3), leads to a more complicated dependence:

$$[O_2^{2-}] = k_1 pO_2^{1/2} pCO_2^{-1} \tag{5}$$

$$[O_2^-] = k_2 pO_2^{3/4} pCO_2^{-1/2} \tag{6}$$

$$[CO_4^{2-}] = k_3 pO_2^{1/2}, \tag{7}$$

where O_2^{2-}, O_2^- and CO_4^{2-} represent the concentration of peroxide, superoxide and percarbonate ions, respectively. The total concentration of dissolved oxygen is therefore here better expressed as a simple molar concentration (mol dm^{-3}) under specified oxygen and CO_2 pressures.

2. Experimental

The equipment, experimental and analytical techniques have been described previously [1,2]. Three binary (Li–Na, Li–K and Na–K) and the ternary (Li–Na–K) carbonate eutectics were used as solvents. Several experiments were performed in Na_2CO_3–NaCl eutectic and in melts based on the ternary carbonate eutectic

with added alkali metal chlorides. Depleted uranium dioxide was provided by British Nuclear Fuels plc (BNFL). Around 1.5 g of UO_2 and 12–15 g of carbonate mixtures were used in each experiment. The melt was first thermostatted at a desired temperature and then air, oxygen, or argon–oxygen mixtures (blended in the required proportion using a Matheson multi-channel mass flow controller (Union Carbide)) were passed through the melt using an alumina bubbler tube. We had previously found that 5–10 h were sufficient for the system to equilibrate and that all the UO_2 that it was possible to oxidise had been oxidised.

The concentrations of uranium(VI) species formed were determined spectrophotometrically. The method is based on the reaction of uranium(VI) with Arsenazo I, and allows the determination of ppm levels of uranium [1]. A weighed sample of the quenched melt, containing uranates and unreacted UO_2, is first treated with dilute (ca. 1M) sulfuric acid, which readily dissolves uranates but does not attack UO_2. The concentration of uranium in the solution thus corresponds to the amount of uranates present in the sample and thus there is no need for a separate redox determination of the different oxidation states of uranium.

3. Results and discussion

3.1. Influence of melts composition

Oxygen solubility in alkali carbonate melts depends on the cationic composition of such media [18]. The dissolution of oxygen leads mainly to the formation of peroxide and superoxide species (reactions (1) and (2)). The presence of lithium favours the formation of peroxide ions but superoxide species are predominantly formed in potassium-rich melts. Yamada et al. [19] found that the concentration of superoxide species in a $(Li–Na)_2CO_3$ melt was about half of that in a $(Li–K)_2CO_3$ melt. Oxygen solubility is therefore expected to be greater in melts containing large concentrations of potassium ions, compared with lithium-rich melts. Anionic composition also affects oxygen solubility. Appleby and Van Druen [8] reported that oxygen solubility in Na_2CO_3–NaCl eutectic (60 mol% Na_2CO_3) is greater than in any carbonate melt studied, and we also found that oxidation of UO_2 could be enhanced by adding alkali metal chloride into the ternary carbonate eutectic melt [2].

Fig. 2 shows the reported total oxygen solubility in a variety of carbonate eutectics [8,10,11,20,21]. Direct low temperature measurements (i.e., below 650°C for $(Li–K)_2CO_3$ eutectic or below 600°C for $(Li–Na)_2CO_3$ and the ternary eutectics) have been only recently attempted by Nishina et al. [10], using the quenching technique. The results of their measurements in the
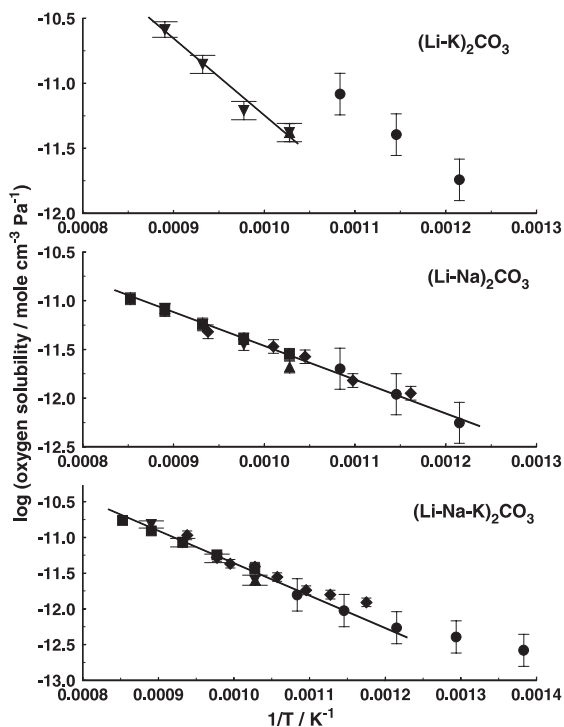
Fig. 2. Total oxygen solubility in A, Li_2CO_3– K_2CO_3 eutectic (1:1.125 mol); B, Li_2CO_3–Na_2CO_3 eutectic (1.14:1 mol) and C, Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic (1.69:1.14:1 mol). Data for ▼, Appleby and Van Druen [8]; ●, Nishina et al. [10]; ■, Janz [21]; ▲, Maru [20] and ◆, Schenke et al. [11].

$(Li–Na)_2CO_3$ melt are in excellent agreement with those reported previously [8,20,21]. However, Fig. 2 shows that the data obtained by Nishina et al. [10] at low temperatures in the ternary eutectic and, especially, in the $(Li–K)_2CO_3$ melt are substantially higher than might be expected on the basis of the data reported in previous studies. There is almost an order of magnitude difference between the various results for the $(Li–K)_2CO_3$ eutectic.

3.2. Henry's law and molal concentrations

In all the above studies, the total oxygen solubility was reported in terms of Henry's law constant (h_c, mol dm^{-3} atm^{-1}). The influence of oxygen partial pressure on solubility has been identified above. However, expressing the concentration of dissolved oxygen in molarity units is not always possible. For molten salts, and especially for melts having mixed composition, the mass rather than the volume of the melt is recorded, and the necessary conversion data on the densities of molten salt mixtures are not always available. It is therefore easier to use the molal, or some similarly expressed, concentration of a solute (e.g., mol g^{-1}). Moreover, strictly speaking, Henry's law demands molality and not the

molar concentration of dissolved gas [22], and therefore expressing the concentration of the solute in moles per mass unit instead of a volume unit allows a more accurate calculation of the temperature dependence of oxygen solubility, according to the general equation

$$\log([O]) = A + BT^{-1},\tag{8}$$

where A and B are constants, and T is the absolute temperature.

For the present work it was possible to convert the reported data [8,10,11,20,21] on oxygen solubility in carbonate melts from molar to molal units using the data on the densities of carbonate mixtures summarised by Janz and Tomkins [23]. When the oxidative capability of various carbonate melts towards uranium dioxide powder, M, (expressed as the mass of UO_2 that could be oxidised in 1 g of air-bubbled melt at the desired temperature) was compared with data available on oxygen solubility, an excellent correlation was found between these two parameters from 450°C to 800°C (Fig. 3). Data for the ternary eutectic below 550°C were extrapolated using Eq. (8). Fig. 3 shows that there is an unambiguous correlation between oxygen solubility and the mass of UO_2 oxidised in carbonate melts and carbonate melts containing added chloride.

For the numerical calculation of this dependence, the following method was adopted. For the ternary eutectic melts, the relationship between the mass of UO_2 oxidised in 1 g of the carbonate mixture (M, g) and temperature was established as

$$M = -0.140(\pm0.004) + (2.33 \pm 0.13)10^{-5}T,$$
$$(r = 0.964).\tag{9}$$
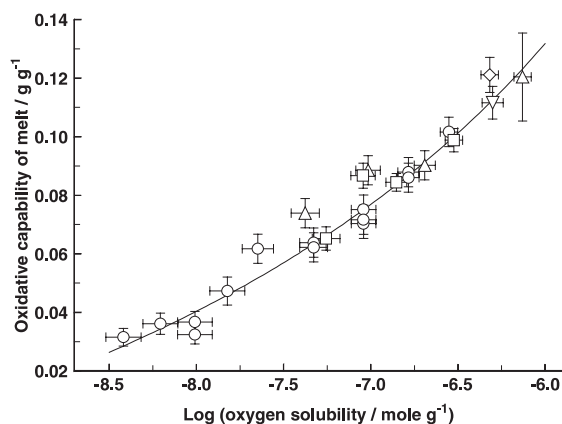

Fig. 3. Relationship between the oxidative capability of carbonate melts towards uranium dioxide powder (mass of UO_2 that 1 g of air-bubbled melt is capable of oxidising) and the total solubility of oxygen. Melts used: ○, $(Li–Na–K)_2CO_3$ eutectic; □, $(Li–Na)_2CO_3$ eutectic; △, $(Li–K)_2CO_3$ eutectic; ▽, $(Na–K)_2CO_3$ melt and ◇, Na_2CO_3–NaCl eutectic.

For oxygen solubility ($[O]$, mol g^{-1}), on averaging data available from the literature [8,10,11,20,21] we obtained

$$\log([O]) = -2.055(\pm 0.001) - 4602(\pm 3)T^{-1}. \tag{10}$$

Using (9) and (10), the following relationships were derived:

$$M = -0.14 - 1.072(2.055 + \log([O]))^{-1} \tag{11}$$

$$\log([O]) = -2.055 - 1.072(M + 0.14)^{-1}. \tag{12}$$

The line in Fig. 3 represents Eq. (11) and shows good agreement between the calculated and experimental results, $M_{calc.}$ and $M_{exp.}$, respectively. For all melt compositions studied the overall correlation coefficient, r, was 0.956.

3.3. Effect of added chloride

We had previously found [2] that oxidation of UO$_2$ powder increased when alkali metal chlorides were added to the ternary carbonate melt. The above technique was thus also used for determining the total oxygen solubility in the ternary carbonate melts containing added chlorides. Table 1 presents the values of oxygen solubility in chloride-containing carbonate melts, calculated using Eq. (12), and measured values of the oxidative capabilities (M) of these ionic media. Non-uniformity of the melt composition again affected the precision of these measurements since the concentration of peroxide/superoxide species formed in carbonate melts with added chloride varies linearly with the concentration of the chloride present [2], Fig. 4. However, the absolute error in these measurements is 2 to 5 times *less* than that reported by Nishina et al. [10] for their low temperature measurements. The data in Table 1 show that the solubility of oxygen at 550°C decreases with increasing radius of the alkali metal cation of the chloride added, in agreement with the previously observed trend for aqueous solutions of alkali metal chlorides [24,25].

The temperature dependence of the oxygen solubility in ternary carbonate melts containing ca. 14 mol%
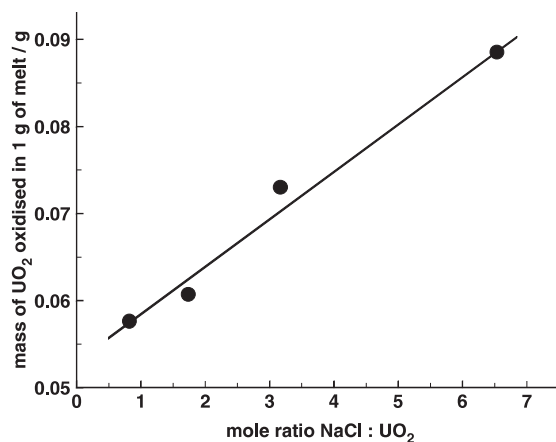

Fig. 4. Effect of NaCl initial concentration on the oxidation of UO$_2$ in (Li–Na–K)$_2$CO$_3$–NaCl melts at 550°C bubbled with air.

added sodium chloride was calculated using the data presented in Table 1. The data fitted a linear relationship according to

$$\log([O]) = -1.9(\pm 0.1) - 3890(\pm 412)T^{-1},$$
$$(r = 0.967). \tag{13}$$

3.4. Influence of oxygen partial pressure

Bubbling oxygen instead of air through ternary carbonate eutectic melts increased the oxidation of added uranium dioxide powder [1]. Eqs. (5)–(7) show that the concentration of the oxidising species formed in molten carbonates increases with increasing oxygen partial pressure, pO_2.

The effect of the partial pressure of oxygen on the dissolution of O$_2$ in molten alkali metal carbonates has been previously studied, generally by electrochemical methods [14–16,24]. Many and varied results have been reported, depending on the melt composition, temperature and even the technique used for the measurements. The value of n in

Table 1
Estimated total oxygen solubility in (Li–Na–K)$_2$CO$_3$–MCl melts

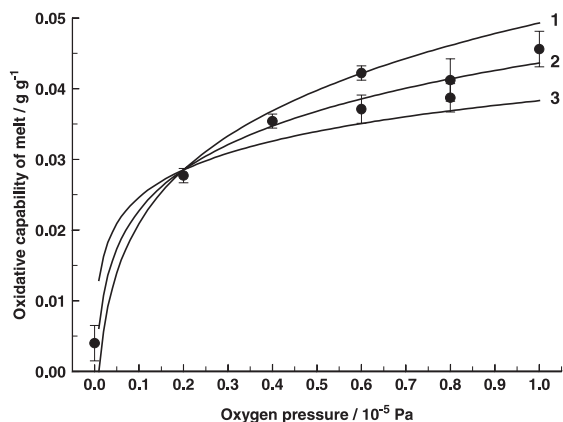| Alkali metal chloride (MCl) added	Concentration of MCl (mol%)	Temperature (°C)	Oxygen solubility 10^6 (mol g^{-1})
NaCl	14.2	450	0.05±0.05
NaCl	14.1	500	0.11±0.07
NaCl	14.2	550	0.33±0.09
NaCl	14.7	600	0.46±0.03
NaCl	14.3	650	0.64±0.10
LiCl	14.6	550	0.38±0.06
CsCl	12.9	550	0.25±0.05

Fig. 5. The effect of the partial pressure of oxygen on the oxidation of UO_2 powder in the ternary carbonate eutectic melt at 450°C under $Ar–O_2$ atmosphere. Symbols show experimental results. Lines represent expected behaviour if oxygen dissolves in the melt forming 1, molecular species, Eq. (1); 2, superoxide species, Eq. (3) and 3, peroxide species, Eq. (2).

$$[O] = KpO_2^n pCO_2^m \tag{14}$$

ranged from 0.16 in $(Li–K)_2CO_3$ eutectic at 700°C–800°C to 0.75 in molten $(Na–K)_2CO_3$ at 800°C.

A series of preliminary experiments were performed on the oxidation of UO_2 powder under an argon–oxygen atmosphere at various partial pressures of O_2 at 450°C. Under these conditions the partial pressure of CO_2 in the atmosphere above the melt was maintained only by the thermal decomposition of the carbonate melt, which was equal to the equilibrium dissociation pressure of the ternary carbonate eutectic. Since all the experiments were performed at the same temperature the value of pCO_2 also remained constant and therefore pCO_2^m was also constant. The results, and their error bars, of these experiments are plotted as oxidative capability of the melt against oxygen partial pressure in Fig. 5. The three curves in the figure represent the oxidative capability of the melt calculated for individual oxygen species, superoxide, peroxide and O_2, in the melt.

3.5. Oxygen species predominating in carbonate melts

Eq. (11) was used to calculate the possible influence of oxygen partial pressure on the oxidative capability of the melt towards uranium dioxide (we neglect the partial pressure of CO_2 since it is constant, see above). From Eq. (14) it follows that

$$\log([O]) = \log(KpO_2^n) = \log(K) + n \; \log(pO_2) \tag{15}$$

and if at 450°C and $pO_2 = 10^5$ Pa then $\log([O]) = \log(K) = -8.418$ (if oxygen solubility in the melt is expressed in mol g^{-1}, Eq. (10)). Eq. (11) was derived for melts saturated with oxygen in air at $pO_2 = 0.23 \times 10^5$

Pa, $(pO_2^{calib.})$, and the corresponding correction was therefore included as necessary. Combining Eqs. (11) and (15), the following dependence was obtained:

$$M = -0.14 - 1.072\{2.055 - \log(K) \\ + n \; \log(pO_2/pO_2^{calib.})\}^{-1}. \tag{16}$$

Using Eq. (16) and varying the value of the parameter n it was possible to calculate the expected oxidative capability of ternary carbonate melts at various partial pressures of oxygen, assuming that for physical molecular dissolution $n = 1$; for superoxide species formation, $n = 0.75$; and for peroxide species formation, $n = 0.5$. The results of these calculations are shown in Fig. 5 as lines 1, 2 and 3, respectively. Our experimental data are closest to line 2, thus supporting the assumption of preferable superoxide formation in the ternary carbonate eutectic at 450°C. This finding is in agreement with the conclusion of Moutiers et al. [17] concerning the stabilisation of superoxide species in moderately acidic carbonate media (low temperatures) and agrees with the report of Smith et al. [12] who found superoxide species in the ternary carbonate eutectic melt at 650°C. It however disagrees with some earlier work (see [16] in Reeve [26]) and Claes [27,28]) that proposed predominantly only peroxide formation, based on electrochemical measurements: the way conclusions are drawn from such measurements must now be reassessed.

3.6. Analytical applications and some limitations

We have therefore shown that the reaction of UO_2 with the oxygen species dissolved in alkali metal carbonate and carbonate-based melts is suitable for straightforward measurements of the concentration of oxygen species formed in such melts. In addition, the predominant species formed has been characterised, Fig. 5, by measuring the dependence of oxygen solubility on the partial pressure of O_2 in the atmosphere.

This method is thus suitable for the determination of oxygen solubility in a range of melt compositions, including sulfate and carbonate-sulfate melts, or in any melt, provided that oxygen is the only available oxidising agent in the system. The method cannot be applied, for example, to nitrate melts where the rate and extent of UO_2 oxidation depends primarily on the concentration of nitrate. Neither can it be applied to molten chlorides bubbled with chlorine, since the formation of uranyl chloride by

$$UO_2 + Cl_2 \rightarrow UO_2Cl_2 \tag{17}$$

predominates over the oxidation of UO_2 by oxygen,

$$4UO_2 + 4MCl + 3O_2 \rightarrow 2M_2U_2O_7 + 2Cl_2 \tag{18}$$

when chlorine is in excess. The method is also not applicable to melts where UO_2 can be dissolved, e.g., melts

with added $AlCl_3$ [2], since in such systems there is no heterogeneous reaction, and the initially formed soluble uranium(IV) complexes are then oxidised by the dissolved oxygen species.

4. Conclusions

A new sensitive method for determining the amount of oxygen taken up by a molten carbonate-containing melt has been established. This method is a variant of a redox titration where an excess of reducing agent (UO_2) is added and the amount of consumed U(IV) is subsequently determined. A quantitative method has been developed for relating the amount of oxygen entering a melt and the melt analysis for the concentration of U(VI) formed. This then allows the determination of low concentrations of oxygen at temperatures well below 550°C (e.g., in the ternary carbonate eutectic melt at 450°C where the solubility of oxygen is around 10^{-8} mole g^{-1}).

The method is based on the reaction of uranium dioxide with the oxygen species (peroxide and superoxide) formed in alkali metal carbonate and carbonate-based melts to produce alkali metal uranates(VI). The extent of the reaction is controlled by oxygen solubility in the melts and the quantitative dependence derived is related to the amount of UO_2 oxidised in a given carbonate melt under chosen conditions and the oxygen solubility in the same melt.

Acknowledgements

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