

# Electrowinning magnesium from its oxide in a melt containing neodymium chloride

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Received 14 May 1995; revised 19 September 1996

A new process for the electrolytic production of magnesium from its oxide is described, based on the reaction  $\text{MgO} + \text{NdCl}_3 \rightarrow \text{MgCl}_2 + \text{NdOCl}$ . This is followed by electrolysis of the resulting  $\text{MgCl}_2/\text{NdCl}_3/\text{NdOCl}$  melt using a carbon anode, the proposed electrolysis reaction being  $2\text{MgCl}_2 + \text{C} + 2\text{NdOCl} \rightarrow 2\text{Mg} + \text{CO}_2 + 2\text{NdCl}_3$ . XRD studies confirm the formation of  $\text{NdOCl}$  when  $\text{MgO}$  is fused with  $\text{NdCl}_3$ . Electrolysis of the melt, using a molten tin cathode and a graphite anode, produced a gas containing chlorine, suggesting some direct electrolysis of chlorides. At  $700^\circ\text{C}$  only chlorine was found, but at  $750^\circ\text{C}$  and above chlorine and carbon dioxide were evolved, the chlorine:carbon dioxide ratio decreasing markedly as the current density was decreased from  $3600$  to  $890 \text{ A m}^{-2}$ . This was consistent with the measured cell voltages, which at  $750^\circ\text{C}$  and above fell below the calculated decomposition voltage of  $\text{MgCl}_2$  at current densities of less than  $1000 \text{ A m}^{-2}$ . There is extensive co-deposition of neodymium with the magnesium with the molten tin cathode, but when magnesium metal was equilibrated with the  $\text{MgCl}_2/\text{NdCl}_3/\text{NdOCl}$  melt only  $0.5 \text{ wt } \%$  of neodymium entered the metal.

## 1. Introduction

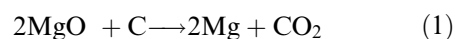
### 1.1. Electrolysis with an oxide feed

Most magnesium is produced by electrolysis of the molten chloride in an electrolyte consisting of alkali metal and alkaline earth metal chlorides [1, 2]. The majority of these processes require anhydrous magnesium chloride as the feed, and it is reported that 50% of the total energy input required is expended in the production of the anhydrous material [3]. The relatively high cost of producing the anhydrous chloride has led to the oxide being considered as a possibly less expensive cell feed. The principal difficulty in using the oxide is its low solubility in chloride or fluoride melts.

Early attempts [4, 5] to employ a magnesium oxide feed involved suspending a mixture of oxide and carbon in a chloride electrolyte; the primary reaction is then electrolysis of the chloride, the anodically-generated chlorine reacting with the carbon and  $\text{MgO}$  to regenerate magnesium chloride. Short-term current efficiencies of 70% were reported with a solid cathode [4] and 90% with a molten pool cathode [5], but the formation of sludges containing  $\text{MgO}$  and carbon eventually interfered with cell operation.

Withers and Loutfy [6] overcame the low solubility of the oxide in conventional melts by incorporating it into a prebaked composite anode consisting of 85 wt%  $\text{MgO}$  and 15 wt% carbon.

Current efficiencies of up to 92% were obtained using this consumable anode and cell voltages were low as the standard decomposition voltage for the cell reaction:



is approximately 1.5 V as compared to the 2.5 V required for magnesium chloride. No difficulty with sludge formation was experienced if a fluoride electrolyte was used. The major difficulty reported was the low conductivity of the composite anode mix, and magnesium rods or strips had to be incorporated into the anode to obtain satisfactory conductivity.

More recently, Sharma [7] has suggested a process in which magnesium is recovered by electrolysis of its oxide. The  $\text{MgO}$  is dissolved in a rare-earth chloride electrolyte, followed by electrolysis between a mild steel cathode and a carbon anode, to produce magnesium metal at the cathode and carbon monoxide or dioxide at the anode, the anode being consumed during the reaction. The process is thus analogous to the Hall–Heroult process for aluminium production in that an oxyhalide species (oxychloride in this instance, oxyfluoride in the aluminium process) reacts with the carbon of the anode to produce  $\text{CO}_2$ . It is likely that this will require an appreciable overvoltage at the anode, and it is of interest that a value of approximately 0.5 V is reported for the aluminium process [8].

The present work is concerned with a preliminary examination of the proposed process.

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### 1.2. Use of neodymium chloride-based electrolytes

In the process as described [7], magnesium oxide is claimed to react with a neodymium chloride/magnesium chloride melt to form neodymium oxychloride and magnesium chloride, as shown by Equation 2:



The MgO/NdCl<sub>3</sub>/MgCl<sub>2</sub>/NdOCl system has been studied by Permyakov *et al.* [9], who present a fusion diagram for the system and state that the standard free energy change for the reaction represented by Equation 2 is  $-2.9 \text{ kJ mol}^{-1}$  at 800 °C. The value of the standard free energy change was also calculated using the CSIRO/Monash Thermochemistry system, the individual  $\Delta G^0$  values at 800 °C for MgO, NdCl<sub>3</sub>, MgCl<sub>2</sub> and NdOCl being  $-484.6$ ,  $-787.2$ ,  $-474.3$  and  $-813.4 \text{ kJ mol}^{-1}$ , respectively. These give a free energy change for Equation 2 of  $-16 \text{ kJ mol}^{-1}$ . This value differs somewhat from that given in [9], but both are slightly negative, supporting the suggestion that NdOCl can be formed by the reaction of MgO and NdCl<sub>3</sub>.

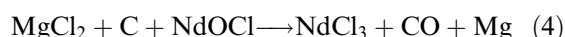
In a very recent study [10] it has been confirmed that MgO is quite soluble in MgCl<sub>2</sub>/NdCl<sub>3</sub> melts. These investigators found, however, a much lower solubility for NdOCl in MgCl<sub>2</sub> than was reported by Permyakov *et al.* [9], and this may mean that the NdOCl concentrations reported in [9] for the three-component melt are too high, especially at low NdCl<sub>3</sub> concentrations. This discrepancy is further discussed in the concluding section.

Similar reactions are possible between MgO and yttrium trichloride [9] or lanthanum trichloride [11], but the neodymium system appears to be the most favourable as it offers lower fusion temperatures and higher solubility of the oxychloride in the melt. For example, the fusion diagram presented in [9] shows that systems melting below 700 °C can be prepared which contain 25 mol% of NdOCl. Consequently the neodymium system was selected for the present study.

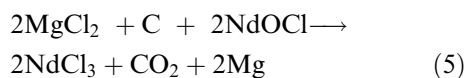
When the MgCl<sub>2</sub>/NdCl<sub>3</sub>/NdOCl melt is electrolysed between an inert cathode and a carbon anode magnesium should be deposited at the cathode by the reaction:



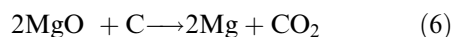
It is further proposed in [7] that the NdOCl formed in Equation 2 will react with the carbon of the anode, giving as the overall cell reaction, for a CO product:



or, if CO<sub>2</sub> is produced,



The neodymium trichloride regenerated in Equation 4 or Equation 5 can react with further MgO as indicated in Equation 2, to give an overall process reaction, for a pure CO<sub>2</sub> product, of



The anode would be consumed in this reaction, the theoretical consumption being  $0.25 \text{ kg kg}^{-1}$  of metal if CO<sub>2</sub> is the sole product, rising to  $0.5 \text{ kg kg}^{-1}$  if only CO was formed.

The cell voltage for Reaction 5, calculated at unit activity of the reactants and 750 °C, is  $-1.65 \text{ V}$  (CSIRO/Monash Thermochemistry system). This may be compared with the standard decomposition voltage for MgCl<sub>2</sub> of  $-2.49 \text{ V}$  [12], and for NdCl<sub>3</sub> of  $-2.72 \text{ V}$ . These voltages are the theoretical standard values, and it is likely that the reactions represented by Equations 4 and 5 would show appreciable overpotential at the anode.

A first evaluation of the proposed process can conveniently be divided into three sections, namely:

- (i) confirm that MgO reacts with neodymium trichloride to form the oxychloride.
- (ii) study the anode reaction products. The gas produced should consist principally of carbon monoxide or dioxide with little chlorine being present.
- (iii) analyse the cathode product for neodymium content.

These three areas have been studied briefly, with the results given below.

## 2. Melt preparation: the MgO–NdCl<sub>3</sub> reaction

### 2.1. Experimental details

The magnesium oxide was BDH AR-grade material, calcined at 600 °C. Magnesium chloride and neodymium trichloride were anhydrous compounds, the magnesium chloride being Sigma 98% material, dried by heating under HCl gas at 400 °C. Volumetric analysis showed an acid consumption equivalent to 0.08 wt% MgO or 0.3 wt% Mg(OH)Cl, while the MgCl<sub>2</sub> content as derived from magnesium analysis (volumetric by EDTA) was 99.9%. The neodymium trichloride was prepared by dehydration of the hexahydrate [13]. Volumetric analysis for neodymium (by EDTA [14]) and for chloride (Volhard procedure) established a chloride/neodymium mole ratio of 3.00, while the sum of the chloride and neodymium content was 99.9%. These results indicate a low NdOCl and water content. All these materials were stored and handled under dry argon ( $\sim 25 \text{ ppm}$  water) in a Vacuum Atmospheres (VA) glove-box.

Selection of the melt composition was based on the fusion diagram presented by Polyakov *et al.* [9]. The three criteria for selection were (i) a low liquidus temperature such that fluid melts would be obtained between 700 and 750 °C, the usual operating temperature limits for magnesium cells, (ii) the NdOCl concentration should be as high as is consistent with (i), to promote reaction of the NdOCl with the carbon of the anode, and (iii) there should be an excess

of  $\text{NdCl}_3$  over that required to react with the  $\text{MgO}$  to favour complete reaction of the oxide. Therefore, the first melt used an  $\text{MgO}/\text{MgCl}_2/\text{NdCl}_3$  mixture calculated to produce a melt of nominal composition 65 mol%  $\text{MgCl}_2$ , 25 mol%  $\text{NdOCl}$  and 10 mol%  $\text{NdCl}_3$ , which should have a liquidus of 650 °C [9]. A second test used an initial mixture calculated to produce a 60 mol%  $\text{MgCl}_2/34$  mol%  $\text{NdOCl}/6$  mol%  $\text{NdCl}_3$  melt. This relatively small change in composition increases the expected liquidus to 710 °C.

A 58 mm (ID)  $\times$  120 mm (high) graphite crucible was used, in a vertical silica tube closed at one end. The tube was flanged at the top to take a standard Quickfit MAF1/75 reaction vessel cover, and a silicone rubber gasket was fitted to ensure a gas-tight seal. An alumina thermocouple sheath and a silica argon inlet tube were introduced through screw-thread-to-cone adaptors. The crucible rested on a fire brick support. The assembly was heated in a vertical tube furnace.

Approximately 300 g of the desired mixture was melted under argon, the melt temperature being taken to 760 °C (first test) or 790 °C (second test) and held for 1 to 2 h to ensure complete fusion. The system was then allowed to cool overnight under argon, the crucible containing the frozen melt transferred to the glove-box as rapidly as possible, and the melt broken out of the crucible. A 5 to 10 g sample was reserved for XRD examination, the bulk of the melt being retained for use in the scoping electrolysis trials described below. The composition of the two melts prepared are listed in Table 1, the final composition being that calculated for complete reaction of the  $\text{MgO}$ .

X-ray diffraction (XRD) data were collected using either a Philips PW1050 goniometer fitted with a PW 1710 controller or a Philips X'PERT powder XRD system incorporating a 3710 goniometer. Both systems employed a copper target. Phase identification was made using the CSIRO Division of Soils XPLOT software. Hygroscopic materials were loaded into sample holders under dry argon, and transferred to the XRD equipment in argon-filled desiccators. The sample was covered with a film of Mylar to minimize water uptake during the XRD scan.

## 2.2. Results

The XRD traces for the products of the two melts were compared to that of a mechanical mixture

Table 1. Melt composition for XRD examination

Component	First melt		Second melt	
	Taken /mol%	Final comp'n /mol%	Taken /mol%	Final comp'n /mol%
$\text{NdCl}_3$	35	10	40	6
$\text{MgCl}_2$	40	65	26	60
$\text{MgO}$	25	nil	34	nil
$\text{NdOCl}$	nil	25	nil	34

containing 35 mol%  $\text{NdCl}_3$ , 40 mol%  $\text{MgCl}_2$  and 25 mol%  $\text{MgO}$ . The XRD results for this mixture and for the first melt are compared in Figs 1 and 2; the results for the second test were similar to those of the first.

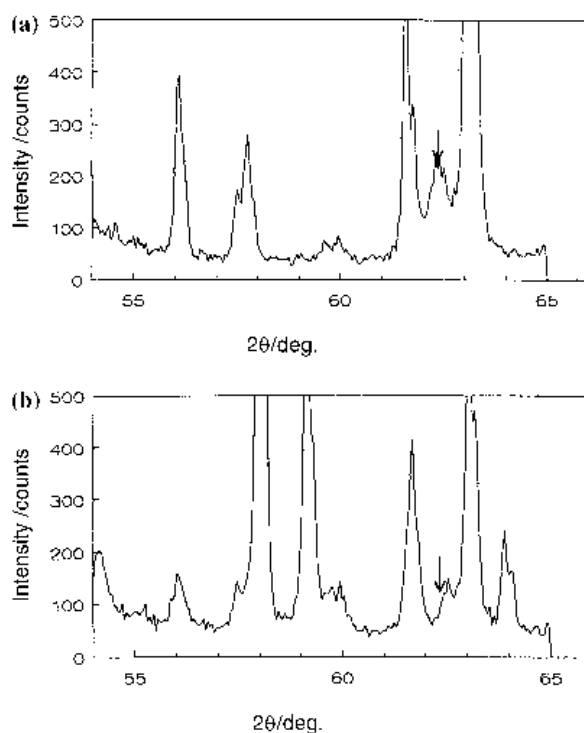


Fig. 1. XRD trace showing  $\text{MgO}$  consumption. (a) initial  $\text{MgO}/\text{MgCl}_2/\text{NdCl}_3$  mixture, (b) melt product from the first test. The arrow marks the position of the 62.4° line for periclase.

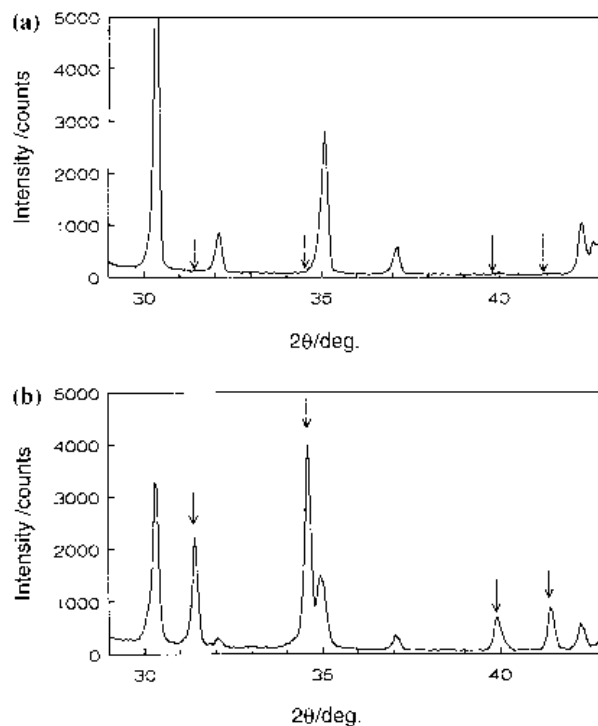


Fig. 2. XRD trace showing  $\text{NdOCl}$  formation. (a) initial  $\text{MgO}/\text{MgCl}_2/\text{NdCl}_3$  mixture, (b) melt product from the first test. The arrows mark the positions of the 31.4°, 34.6°, 39.9° and 41.4° peaks for  $\text{NdOCl}$ .

In examining the XRD scans for the presence of MgO (periclase), the more prominent peaks for MgO are masked by peaks generated by  $\text{NdCl}_3$ , and only the relatively weak reflection at a  $2\theta$  value of  $62.4^\circ$  is free of interference. Comparing the results shown in Fig. 1(a) and (b), this MgO peak is visible in the initial mixture, but is not detectable in the melt product. It is also clear that the sensitivity for MgO detection is relatively poor.

The appearance of NdOCl is more distinct, as is shown in Fig. 2(a) and (b). Considering the major NdOCl peaks at  $2\theta$  values of  $31.4^\circ$  and  $34.6^\circ$ , it can be seen that there is insufficient NdOCl present in the unreacted material to produce a visible peak, but that after melting NdOCl appears as a major component. The disappearance of MgO from the melt product, and the simultaneous appearance of NdOCl as a major component, supports the suggestion that the reaction described by Equation 2 is taking place. However, the appearance of NdOCl in the solidified melt does not prove that the oxychloride formed was completely soluble in the melt, nor does it indicate whether the NdOCl is present in the melt as such, or as complex species formed between NdOCl and  $\text{NdCl}_3$ . Despite these uncertainties it was decided to carry out some electrolysis trials.

### 3. Electrolysis

Magnesium metal (density:  $1.56 \text{ g cm}^{-3}$  at  $750^\circ\text{C}$  [2]) being less dense than the melt ( $\sim 2.6 \text{ g cm}^{-3}$ ), would float to the surface during electrolysis. In a simple cell the metal would be likely to react with the anode gases. To prevent this, and retain a simple cell construction, it was decided to work with a molten pool cathode, selecting a metal more dense than the electrolyte which forms liquid alloys with magnesium at electrolysis temperature. Tin was used in most of this work.

Two electrolysis trials were made to refine the equipment and techniques required. In the first, performed at  $700^\circ\text{C}$  using the first melt described above, a tin cathode and a graphite anode were used. Considerable chlorine was evolved, the anode showed no loss in weight (0.67 g expected from Equation 5), and there was extensive codeposition of neodymium with the magnesium. In the second, made at  $775^\circ\text{C}$  and using the second melt and a zinc cathode, chlorine was again detected, the current efficiency for chlorine production being 62.1%. There was again considerable codeposition of neodymium and magnesium. The anode was not recovered intact and its weight loss could not be determined.

These initial tests showed that chlorine was a major anode product, and a further set of electrolysis trials were performed to more closely define the chlorine/carbon dioxide ratio produced at the anode. For simplicity, the molten pool cathode cell design was retained, even though the initial tests had shown that considerable neodymium was codeposited.

#### 3.1. Equipment and reagents

The cell comprised a cylindrical crucible of recrystallized alumina, 60 mm (ID)  $\times$  140 mm (deep), the tin cathode pool being approximately 10 mm deep and required about 160 g of tin. Electrical contact to this pool was by a 3 mm (dia.) tantalum wire, sheathed in a loose-fitting alumina tube, sealed at the top with silicone putty and at the bottom with Sauereisen no. 8 cement, a proprietary product containing zirconium silicate. The anode was usually of Morganite EY941 graphite, but other materials were evaluated. All anodes were 15 mm (dia.) cylinders, 60 mm high, with a shallow conical bottom as shown in Fig. 3. Three alumina pins ensured clearance from the crucible wall. The anode was supported by a bare 6 mm (dia.) graphite rod. Unless otherwise stated the anode was immersed 20 mm into the melt, giving a working area of  $11.2 \text{ cm}^2$  and an initial anode-cathode separation of 25 mm.

The flanged heating tube, crucible support and cover were as described in Section 2.1. The electrode leads, gas inlet and thermocouple sheath were fed through the cover by use of screw-thread cone adaptors. It was found necessary to use a Viton gasket to withstand the chlorine evolved during the reaction.

The cell was operated under an argon gas cover, the cell head pressure being held at 250 to 500 Pa below atmospheric to minimize loss of any of the gases produced. The cell off-gas was taken through a glass-wool filter to a 30 mm ID absorption column packed with 220 mm of 6 mm Raschig rings. A 1.5 M sodium hydroxide solution was circulated over this packing to absorb both chlorine and carbon dioxide. The system pressure was controlled by means of a small centrifugal blower used in the exhaust mode. Figure 4 shows a diagram of the equipment.

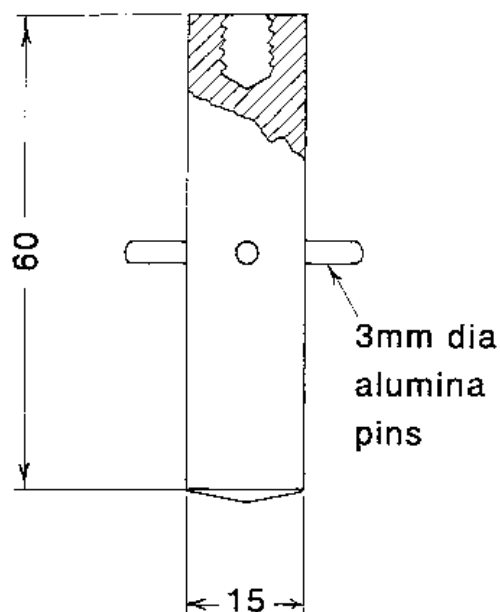


Fig. 3. Diagram of anode construction.

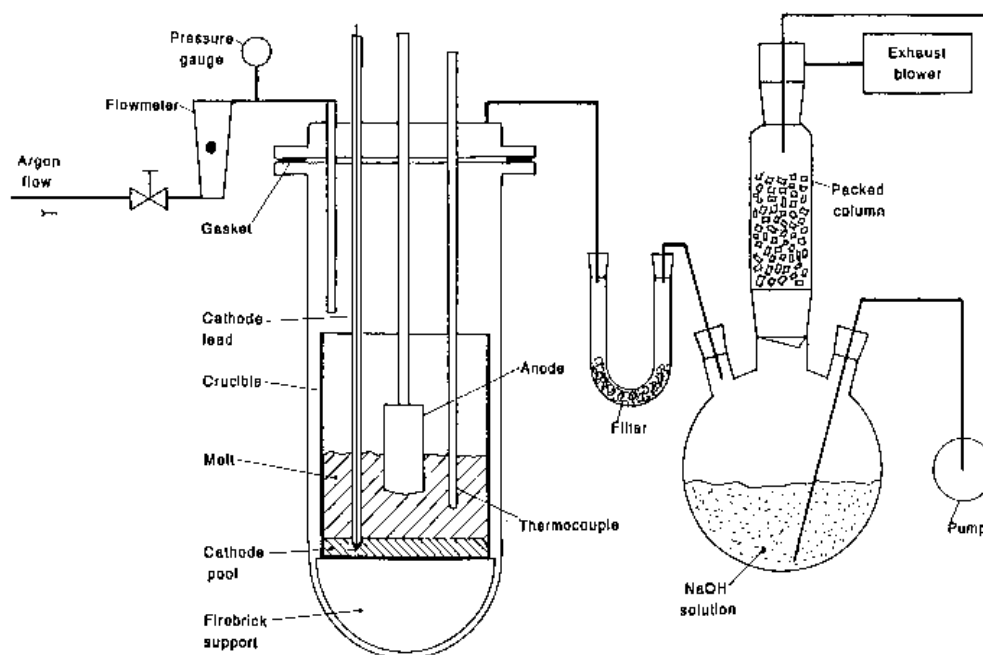


Fig. 4. Diagram of system for electrolysis tests.

For each test 330 g of electrolyte were prepared by mixing magnesium chloride, magnesium oxide and neodymium trichloride (or  $\text{NdCl}_3/\text{NdOCl}$  mixture, see below) to give a 65/10/25 mol% magnesium chloride/neodymium trichloride/neodymium oxychloride melt, assuming complete conversion of the  $\text{MgO}$  according to Equation 2. The  $\text{MgO}$  and  $\text{MgCl}_2$  used were as specified in Section 2.1. For several of the tests it was possible to use the anhydrous neodymium trichloride described above, but there was not sufficient available to perform all the desired tests, and further anhydrous material had to be prepared from the hexahydrate. An anhydrous  $\text{NdCl}_3/\text{NdOCl}$  mixture can be prepared relatively simply by heating the hydrated chloride under argon [13], and since in the present work oxychloride is a component of the melt, the dehydration was terminated at this stage. The product was analysed for neodymium and chloride as described in Section 2.1, and the fraction of  $\text{NdOCl}$  calculated from these values. Typical results were 27–33 mol% for  $\text{NdOCl}$  and 99.8 to 100 wt% for the sum of the trichloride and oxychloride present.

Electrolyses were made galvanostatically, using an instrument developed in these laboratories. The total charge passed was recorded on a coulometer, and the cell resistance estimated by superimposing a small 1 kHz signal on the cell current, and measuring the amplitude and phase angle of the periodic part of the current and voltage. In practice the phase angle was very small (1 to 2°) and hence the resistance was taken as equal to the impedance. Electrolyte temperature was measured with a type K thermocouple, and indicated on a Jenco 767 indicator/transmitter. The cell voltage, resistance and temperature were recorded on a three-pen Rikadenki chart recorder, the

voltage being buffered through a unity-gain differential amplifier

The equipment was tested by performing an electrolysis on a conventional magnesium electrolyte (19 wt%  $\text{MgCl}_2$ , 14 wt%  $\text{CaCl}_2$ , 33 wt% each  $\text{NaCl}$  and  $\text{KCl}$  and 1 wt%  $\text{NaF}$ ) at 700 °C and 4 A (3600  $\text{A m}^{-2}$  anode current density). The current efficiency (CE), from the chlorine absorbed, was 92.9%, which is comparable with previously reported CEs for a similar system [15]. The metal was obtained as a single coherent ingot.

### 3.2. Test procedure

The required reagents were weighed, mixed, and loaded into the crucible under argon in a VA glove box, and the crucible was maintained under argon until placed in the furnace tube, the argon atmosphere being reestablished as soon as the tube was covered. After fusion of the mixture, the cathode contact, the anode and the thermocouple were lowered into the melt, the temperature adjusted as required, and the electrolysis commenced.

Two polarization curves were recorded over the current range 0.25 to 5 A, the first about 30 min after commencement, and the second about 30 min prior to completion. The total charge passed was usually 10 Ah but at the low current density this was reduced to 5 Ah. The test was terminated when the desired charge had been passed, whereupon the cathode contact, anode and thermocouple were withdrawn from the melt. The crucible was then removed from the furnace and the melt cast into a dry graphite mould. The melt was allowed to solidify, cooled in a desiccator, and transferred to the glove-box when cool.

The solidified salt was chipped away from the cathode metal as completely as possible, broken, and samples retained for XRD and chemical analysis. The remainder of the salt was leached in hot water and any residue subjected to repeated ultrasonic agitation and decantation to separate the insoluble oxychloride from any dispersed metal present, as unlike the conventional magnesium electrolysis described above, some of the metal was present in the form of fines. This treatment was repeated until the metal appeared clean and the aqueous phase was clear of suspended material. The cleaned metal was dried at 110 °C, weighed, and screened on a 14 mesh screen to recover a massive coherent fraction, metal fragments and metal fines. Each of these fractions was weighed, sampled, and analysed for neodymium and magnesium by ICP-AES and atomic absorption spectroscopy, respectively.

The fines plus fragments averaged  $34 \pm 3.4$  wt% of the total metal for the runs made at  $3600 \text{ A m}^{-2}$ , 700–750 °C and with 10 Ah of charge passed. This fraction fell to 10 wt% when the temperature was increased to 800 °C, and to 5 wt% at  $890 \text{ A m}^{-2}$ , 750 °C, 5 Ah of charge. The composition averaged 4 wt% Nd in the compact metal, 10 wt% Nd in the metal fragments and 26 wt% Nd in the fines; all fractions contained about 0.5 wt% magnesium. Since considerable neodymium is deposited into the cathode it is suggested that the top layer of cathode metal gradually becomes enriched in neodymium, and forms a granular solid phase. This effect would be minimized with less charge passed and at lower current density, as was observed. The data do not warrant further speculation.

The sodium hydroxide absorption solution plus washings were transferred to a tared container, weighed, and weighed aliquots analysed iodometrically for hypochlorite, and by the barium carbonate precipitation technique [16] for carbonate. A blank carbonate determination was made on the initial absorption solution. An analysis for total chloride was also performed on the final solution after reduction of the hypochlorite with hydrogen peroxide (Volhard procedure). The fraction of the absorption solution recovered was checked by comparing the sum of the alkali and total chloride in the final solution with the total number of moles of alkali

in the initial solution. This ratio should be 1.00 and was found to be  $0.996 \pm 0.004$ .

The anode was detached from the support rod and extracted with dilute acid and hot water to constant weight. After leaching, it was dried at 110 °C and weighed.

### 3.3. Anode gases

Table 2 lists the chlorine and carbon dioxide found by analysis of the absorption solution. In all instances there was an appreciable fraction of chlorine in the cell off-gas, this proportion being dependent on both current density and electrolyte temperature. The effect of current density was substantial, the  $\text{Cl}_2/(\text{Cl}_2+\text{CO}_2)$  mole ratio ('chlorine ratio') at 750 °C decreasing from approximately 70% at  $3600 \text{ A m}^{-2}$  to 28% at  $890 \text{ A m}^{-2}$ . The change in this ratio with change of temperature was also significant, decreasing from 100% at 703 °C through 72% at 750 °C to 64% at 800 °C. This latter value may be high, as an interelectrode short occurred during this test after about 7 Ah had been passed. The short was cleared by raising the anode 10 mm, which would have increased the current density to approximately  $6200 \text{ A m}^{-2}$ . This would probably have increased the proportion of chlorine in the off-gas over this period, leading to a high result for the average chlorine ratio while the short-circuit explains the low CE.

The anode carbon was varied between a pure, high density graphite (EY941,  $1.76 \text{ g cm}^{-3}$ ), a lower density graphite (Le Carbone Lorraine LCL102,  $1.67 \text{ g cm}^{-3}$ ) and a carbon prepared from brown coal char (BCC). There was little variation in the chlorine yield between these carbons, the chlorine ratio ranging from 68 to 73%.

The weight of anode carbon consumed by the reaction may be estimated both from the quantity of carbon dioxide absorbed and the weight loss of the anode, and both these values are listed in Table 3. These weights are comparable except for run 6, which used a more porous graphite and may have taken up more salt. Excluding the values for runs 4 and 6, the measured weight loss averaged a factor of  $1.14 \pm 0.14$  of that estimated from the carbon dioxide found. This difference may represent mechanical loss of unreacted carbon, or may indicate some carbon mon-

Table 2. Chlorine and carbon dioxide in cell off-gas

Run	Temp. /°C	Anode CD /A m <sup>-2</sup>	Anode carbon type	Anode gases			
				Chlorine ratio/%	Current efficiency /%		
					Cl <sub>2</sub>	CO <sub>2</sub>	Total
4	703	3600	EY941	100	96	0	96
5	750	3600	EY941	72	54	42	96
6	750	3600	LCL102	73	54	41	95
7	750	3600	B.C.C	68	48	46	94
9	800	3600	EY941	64	36	42	78
10	750	890	EY941	28	16	79	95

Table 3. Anode consumption

Run	Anode consumption/g	
	Ex wt. loss	Ex CO <sub>2</sub>
4	-0.01	nil
5	0.50	0.47
6	0.26	0.46
7	0.68	0.51
9	0.54	0.47
10	0.45	0.44

oxide formation, but the available data do not allow discrimination between these possibilities. The immersed section of each of the anodes was visibly attacked. Even the anode used in run 4, where there was no significant weight loss and no carbon dioxide found, developed a soft, powdery surface. All others showed a measurable decrease in diameter of the order of 0.5 mm in the immersed section, with no measurable change in the diameter of the section above the melt. Assuming the 0.5 mm decrease in diameter (i.e., 0.25 mm thickness lost) to be uniform over the whole 11.2 cm<sup>2</sup> working area, then for a material of density 1.7 g cm<sup>-3</sup> the weight loss is of the order of 0.5 g. This is close to the measured loss and confirms that it is the immersed carbon that is reacting, rather than oxidation of the section above the melt, or the support rod.

### 3.4. Cell voltage

The cell voltage, corrected for ohmic loss, is shown as a function of current density and electrolyte temperature in Fig. 5. The anode was in all instances EY941 graphite, and the data were recorded after about 8.5 Ah of charge had been passed. The cell voltages, at low current density, ranged from about 2.27 V at 700 °C to 1.8 V at 800 °C. These are between

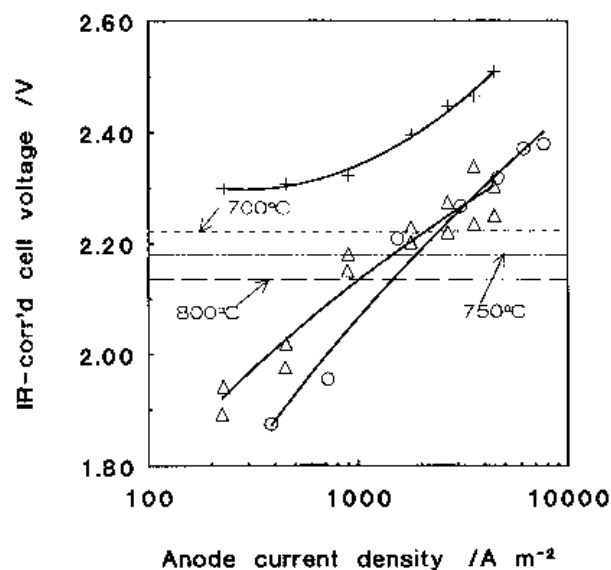


Fig. 5. Cell polarization curves. Key: (+)700 °C, (Δ)750 °C, (○) 800 °C. The broken lines show the MgCl<sub>2</sub> decomposition voltages.

the standard decomposition voltage for magnesium chloride (-2.517 V at 700 °C to -2.459 V at 800 °C [12]) and that for the reaction of Equation 5 of -1.65 V at 750 °C.

This is in part due to the low activity of magnesium in the liquid cathode; the magnesium concentration in the coherent cathode material recovered was approximately 0.5 wt% (0.024 atom fraction), and the activity coefficient for magnesium in tin is approximately 0.025 at low magnesium concentrations [17], giving a magnesium activity of  $6 \times 10^{-4}$ . Assuming the activity of magnesium chloride in the melt is equal to its mole fraction (0.65) and taking the activity of chlorine as unity, the theoretical decomposition voltage ( $E_M$ ) for the liquid cathode cell can be calculated from

$$E_M = E_{\text{MgCl}_2}^0 - \frac{RT}{nF} \ln \left[ \frac{a_{\text{Mg}} a_{\text{Cl}_2}}{a_{\text{MgCl}_2}} \right] \quad (7)$$

where  $R$  is the gas constant,  $F$  the Faraday constant,  $n$  is the electron number of the reaction,  $T$  the temperature (K),  $E_{\text{MgCl}_2}^0$  the standard decomposition voltage of MgCl<sub>2</sub> and  $a_x$  the activity of the species designated in the subscript. For the activity values suggested the value of  $E_M$  ranges from -2.224 V at 700 °C to -2.180 V at 750 °C to -2.136 V at 800 °C.

The experimental values for the cell voltage at 700 °C are all greater than the value of  $E_M$ , approaching 2.27 V at low current density. This would be consistent with the reaction at 700 °C being the electrolysis of magnesium chloride to metal and chlorine, rather than the reaction of Equation 5. This agrees with the observation that only chlorine was produced at this temperature. At 750 °C and 800 °C the value of the cell voltage fell progressively below the value for magnesium chloride decomposition as the anode current density was reduced below 1000 A m<sup>-2</sup>, as shown in Fig. 5. This may indicate that the reaction occurring at low current density at these temperatures was that of Equation 5, and this agrees with the observation that the proportion of CO<sub>2</sub> in the off-gas increased markedly when the current density was reduced, and the temperature increased.

The theoretical decomposition voltage for the reaction of Equation 5 was calculated for the molten pool cathode cell using the magnesium activity estimated above, and taking the activities of MgCl<sub>2</sub>, NdCl<sub>3</sub> and NdOCl as their mole fractions in the melt, the activity of CO<sub>2</sub> as its mole fraction in the gas evolved and the activity of carbon as unity. For the conditions of run 10 (Table 2) this gives a theoretical decomposition voltage of -1.30 V; the  $IR$ -corrected cell voltage at 890 A m<sup>-2</sup> averaged 2.14 V giving a cell overvoltage for Reaction 5 of approximately 0.84 V at 890 A m<sup>-2</sup>. The faradaic efficiency for CO<sub>2</sub> formation at this current density is 79%, equivalent to a current density for CO<sub>2</sub> production of 700 A m<sup>-2</sup>. Since the overpotential for the deposition of magnesium should be low, the major part of the cell overvoltage probably occurs at the anode, indicating a

CO<sub>2</sub> overpotential of 0.84 V at 700 A m<sup>-2</sup>. The corresponding calculation using run 5 data gives a CO<sub>2</sub> overpotential of 0.95 V at 1500 A m<sup>-2</sup>.

### 3.5. Electrolyte composition

The solidified final electrolyte from each test was examined by XRD. Only that from run 5 showed even a small MgO peak, and in all instances a prominent NdOCl spectrum was found.

### 3.6. Cathode metal

Considerable neodymium was codeposited with the magnesium in the molten tin cathode, and in several instances from 30% to 50% of the neodymium reported as a neodymium-rich (25 wt% Nd) finely dispersed phase rather than in the bulk metal. Only about 20% of the charge passed was utilized for magnesium deposition, as shown in Table 4. The overall CE for the deposition of both metals is consistently greater than the overall anodic CE for both chlorine and carbon dioxide production, the average ratio of cathodic to anodic CE being  $1.08 \pm 0.06$ . Further, in many cases the cathodic CE was greater than 100%. No certain reason can be proposed for this; there may have been some inclusion of NdOCl in the recovered cathode material although the final washed product showed no visible inclusions.

If neodymium is to be codeposited with magnesium its activity in the cathode pool must be reduced to a value sufficiently low that the decomposition voltage of NdCl<sub>3</sub> is close to that of magnesium chloride. The standard decomposition potential for NdCl<sub>3</sub>, calculated from thermodynamic data (CSIRO/Monash Thermochemistry system using data from [18]) is  $-2.710$  V at 750 °C, and for codeposition to occur this must be reduced to the  $-2.180$  V of MgCl<sub>2</sub> into the cathode pool.

Taking the activity of NdCl<sub>3</sub> in the melt as its mole fraction (0.10) and the activity of chlorine as unity, the activity of Nd in the cathode metal to give a decomposition voltage of  $-2.180$  is  $1.2 \times 10^{-9}$ . As the concentration of neodymium in the coherent metal is approximately 4 wt% (0.031 atom fraction), the activity coefficient ( $\gamma$ ) for neodymium in tin to give the activity calculated above has a value of  $\log \gamma = -7.4$ . No values for the activity coefficient of neodymium in

molten tin have been found, but neodymium in bismuth has a  $\log \gamma$  of  $-8$  at 600 °C [19] and Bayanov [20] lists the activity coefficients for a number of lanthanides in bismuth and zinc; at 750 °C  $\log \gamma$  ranges from  $-5$  to  $-10$ . Thus the  $\log \gamma$  value required for the co-deposition of magnesium and neodymium into tin falls within the range reported for other lanthanides.

More directly, Zhao *et al.* [21] have measured the deposition potential for neodymium into a number of molten cathodes from a NdCl<sub>3</sub>/KCl/NaCl electrolyte. The cathode potential for deposition into tin, measured against a chlorine reference, was  $-2.25$  V at 800 °C, which is comparable with the decomposition voltage for magnesium chloride into a tin pool, and is therefore consistent with the codeposition of neodymium and magnesium.

## 4. Neodymium in magnesium metal

The high neodymium concentrations found in the cathode metal were observed using a molten pool cathode, and might not occur if a solid cathode were to be used and magnesium liberated as molten metal. There are, however, some reports that magnesium in contact with melts containing neodymium trichloride forms alloys containing from 1 to 10 wt% of neodymium [22, 23]. Accordingly, tests were made to assess the level of neodymium likely to be found in magnesium evolved from a solid cathode.

In the first test 140 g of a mixture calculated to produce a 65/10/25 mol% MgCl<sub>2</sub>/NdCl<sub>3</sub>/NdOCl melt was fused in an alumina crucible under argon using the equipment described above. When the melt had reached 750 °C, 11 g of magnesium metal was added via a drop tube, and the melt agitated by bubbling with argon for 5 min. It was then allowed to stand for 30 min, then cooled overnight under argon. The magnesium metal was recovered from the solidified melt as a single well-defined bright button, which was water-washed and a section cut from the centre for analysis by ICP-AES. It contained 0.52 wt% neodymium.

In a second test magnesium was reacted with a melt containing 49 wt% NaCl, 22 wt% CaCl<sub>2</sub>, 23 wt% MgCl<sub>2</sub>, 1 wt% NaF and 5 wt% NdCl<sub>3</sub>, that is, a conventional magnesium electrolyte with a small concentration of NdCl<sub>3</sub> added to prevent the formation of MgO-based sludges [7]. The procedure was as for the first test, and the metal recovered contained 1.51 wt% neodymium.

It is suggested that the reaction for the deposition of neodymium in magnesium is



The equilibrium constant for this reaction can be estimated from thermodynamic data (CSIRO/Monash Thermochemistry system); at 750 °C it is  $4.27 \times 10^{-4}$ . Considering the MgCl<sub>2</sub>/NdCl<sub>3</sub>/NdOCl melt, and taking the activity of magnesium chloride and neodymium chloride as equal to their molar

Table 4. Cathode current efficiencies

Run	Cathodic CE /%			Ratio cathode CE to anodic CE
	For Nd	For Mg	Total	
4	81	23	104	1.08
5	77	19	96	1.00
6	82	26	108	1.14
7	94	15	109	1.16
9	63	19	82	1.05
10	74	27	101	1.07



fractions in the melt, and the activity coefficient of magnesium metal as unity, the equilibrium activity for neodymium in magnesium is  $8.15 \times 10^{-5}$ . The measured concentration of neodymium in magnesium was 0.52 wt% ( $8.5 \times 10^{-4}$  atom fraction), corresponding to an activity coefficient for neodymium in magnesium of  $9 \times 10^{-2}$ . Again no activity coefficient data could be found in the literature for neodymium in magnesium, but values for yttrium and cerium in magnesium were  $1.4 \times 10^{-2}$  and  $7 \times 10^{-4}$ , respectively [20]. Values of this order of magnitude for neodymium would be more than adequate to explain the concentration found in the magnesium metal.

## 5. Conclusion

Although the present work is a preliminary study, some important features of the proposed process have been established. The XRD studies of the products of fusing  $\text{MgCl}_2/\text{NdCl}_3/\text{MgO}$  mixtures show disappearance of the  $\text{MgO}$  and formation of  $\text{NdOCl}$  as predicted by Equation 2. Electrolysis of the resulting melts, however, does not yield an off-gas consisting solely of carbon dioxide, as required by Equation 5, but produces a gas containing a high proportion of chlorine. The fraction of chlorine is least at lower current densities and at higher temperatures. It appears that at  $700^\circ\text{C}$  only chlorides are being electrolysed, but that at  $750^\circ\text{C}$  and above there is appreciable reaction between  $\text{NdOCl}$  and carbon. Further, there was extensive codeposition of neodymium with the magnesium product. The formation of chlorine, and the presence of neodymium in the product metal, are matters of concern for the proposed process.

In a practical system, any chlorine produced would have to be converted to magnesium chloride and returned to the cell, if the electrolyte composition was to remain invariant. While this chloride need not be oxide-free, the necessity to have some part of the cell feed supplied as magnesium chloride negates the principal advantage of the proposed process, namely the use of  $\text{MgO}$  as feed. Thus the chlorine content of the off-gas must be reduced to a low value if the process is to be feasible. Minimum chlorine is associated with operation at lower current density and at higher melt temperatures. The results obtained in the present work suggest that a current density well below  $1000 \text{ A m}^{-2}$  would be required to reduce the chlorine content to an acceptable value, which implies a large cell and a high capital cost. Therefore, it is useful to seek conditions which will allow cell operation at high current densities without chlorine formation.

The selection of the electrolyte composition employed in this work (nominally 65 mol%  $\text{MgCl}_2$ , 10 mol%  $\text{NdCl}_3$  and 25 mol%  $\text{NdOCl}$ ) was based on the phase diagram reported by Permyakov *et al.* [9]. This diagram is inconsistent with more recent data obtained from a study of the  $\text{MgCl}_2/\text{NdOCl}$  binary system [10], which reports a low value, of the order of

1 mol%, for the solubility of  $\text{NdOCl}$  in  $\text{MgCl}_2$ . Thus, it is possible that the  $\text{NdOCl}$  formed by Equation 2 is only partly soluble in the high- $\text{MgCl}_2$ , low- $\text{NdCl}_3$  melts used in the present work, suggesting that the concentration of the  $\text{NdOCl}$  in the liquid phase may have been lower than expected. An alternative electrolyte composition could overcome this difficulty. For example  $\text{NdOCl}$  is quite soluble in  $\text{NdCl}_3$ , T'ien and Morozov [24] reporting a eutectic composition for this binary of 16.5 mol%  $\text{NdOCl}$  at  $722^\circ\text{C}$ , that is, 16.5 mol% of  $\text{NdOCl}$  is soluble in this melt at  $722^\circ\text{C}$ . Thus, the phase diagram of Permyakov *et al.* [9] may not be in error in the region near this eutectic, and it should be possible to prepare an electrolyte containing 15 to 20 mol% of each of  $\text{MgCl}_2$  and  $\text{NdOCl}$ , and 60 to 70 mol% of  $\text{NdCl}_3$ , with a liquidus of about  $720^\circ\text{C}$ . The high concentration of  $\text{NdOCl}$  in solution in such a melt would favour the reaction of the oxychloride with carbon, minimizing chlorine formation. Such melts would, however, show some increase in ohmic losses during electrolysis due to the lower conductivity of  $\text{NdCl}_3$  [25] as compared to that of  $\text{MgCl}_2$ .

The complex species present in these melts are of interest. Raman spectra studies [26] indicate  $\text{NdCl}_6^{3-}$  complexes in  $\text{NdCl}_3$  based melts, and the present study suggests that  $\text{MgO}$  reacts with  $\text{NdCl}_3$  forming  $\text{NdOCl}$  and  $\text{MgCl}_2$ . It has been reported earlier that complexes such as  $\text{NdOCl}_2^{1-}$  are formed in  $\text{NdCl}_3$  based melts containing  $\text{NdOCl}$  [27]. This conclusion was drawn from the agreement between activities calculated respectively from the Clausius–Clapeyron equation and from Temkin's model using the above complex as one of the ions. Thus, the  $\text{NdCl}_3$  based melts are analogous to the cryolite-based melts employed in alumina electrolysis, where  $\text{AlF}_6^{3-}$  based complexes dissolve alumina with the formation of oxyfluoride complexes [8, 28]. In the aluminium production cell the anodic overvoltage is about 0.5 V and the primary product is  $\text{CO}_2$  [8]. This overvoltage arises because of the difficulty of  $\text{CO}$  evolution from the carbon surface, and the activation energy required for the discharge of a second oxygen to form  $\text{CO}_2$  [8, 28]. It is suggested that the process for  $\text{CO}_2$  formation in the  $\text{NdCl}_3$  based electrolytes may be similar; consequently, the overvoltage of 0.9 V observed for  $\text{CO}_2$  formation seems unduly high. This may be due to a low concentration of soluble  $\text{NdOCl}$  in the present work, as discussed above. In any case, Dewing [28] reports that the  $\text{CO}_2$  overvoltage is lower on carbon than on graphite, and it would appear of interest to study the effect of using a range of carbons of different reactivities on the chlorine/carbon dioxide ratio in the off-gas.

The other principal concern was the co-deposition of neodymium with the magnesium metal product. This was especially noticeable with a molten tin cathode, but should be less severe when a solid cathode is employed. In this case the neodymium content of the product metal should approach the approximately 0.5 wt% found when magnesium me-

tal is contacted with the molten electrolyte. Such metal could be applied directly to the production of magnesium/rare earth alloys. If pure magnesium was required the neodymium-containing metal could be purified, for example by distillation, or possibly by extraction of the neodymium into pure molten  $\text{MgCl}_2$ , Reaction 8 being reversed due to the low concentration of  $\text{NdCl}_3$  in the salt phase.

From the above, possible approaches to minimize chlorine formation would be as follows:

- (i) to carry out the electrolysis at higher temperature, as the carbon dioxide formation is favoured by an increase in electrolysis temperature.
- (ii) to evaluate a range of carbons as anode materials, in the expectation that the  $\text{CO}_2$  overpotential will be smaller on a more reactive carbon.
- (iii) to optimize the electrolyte composition. Only one composition was examined in this study, and it would be useful to evaluate the effect of change in electrolyte composition on the solubility of  $\text{MgO}$  and  $\text{NdOCl}$ , on the  $\text{Cl}_2/\text{CO}_2$  ratio in the off-gas, and on the conductive and other physical properties of the electrolyte.

In addition, it would be necessary to confirm that metal of an acceptable composition can be deposited at a solid cathode, and that this metal coalesces sufficiently to permit collection.

### Acknowledgements

The assistance of L. Rogers and L. Cranswick with the XRD studies is acknowledged, as is that of R. Dorin for making the CSIRO/Monash Thermochemistry system calculations, and that of Ms P. Hoobin and Ms C. McInnes for performing the atomic absorption and ICP-AES analyses.

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