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3,565,917

MAGNESIUM CELL OPERATION

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6 Claims

ABSTRACT OF THE DISCLOSURE

Improved operation of electrolytic cells used in producing magnesium metal is achieved by adding vanadium to the electrolyte. Conveniently the vanadium is added to the cell feed material in an amount of from about 5 to about 300 parts per million by weight based on the total feed and preferably in the range of from about 25 to 175 parts per million. The vanadium is added in the preferred manner as vanadium pentoxide.

BACKGROUND OF THE INVENTION

This invention relates to the production of magnesium by electrolytic means and particularly to cell feed materials for use in such production which contain an additive of vanadium.

In the operation of an electrolytic cell for the production of magnesium the electrolyte ordinarily consists of the chlorides of magnesium and one or more alkali and alkaline earth metals, e.g. lithium, sodium, potassium, calcium and barium. Minor amounts of fluorides of these same metals are advantageous and traces of oxides and salts of other metals, e.g. iron, boron, and manganese can be tolerated.

The relative amounts of the major constituents of the bath are well known to those skilled in the art and are varied depending upon the properties desired for the bath, e.g. electrical conductivity and density.

A representative electrolyte used in the present invention contained 20% magnesium chloride, 21% calcium chloride, 58% sodium chloride and 1% calcium fluoride. This particular bath was used in Examples 5(a) and (c). The remainder of the examples were conducted on baths having compositions within the following ranges:

	Percent
MgCl ₂	1-23
BaCl ₂	0-20
NaCl	0-60
CaCl ₂	0-23
KCl	0-80
CaF ₂	0-2

The operation of such electrolytic cells at high efficiency is a constant aim of those engaged in the production of magnesium by electrolytic means.

Accordingly, a principal object of this invention is an improved cell bath composition.

Another object of this invention is to provide a cell bath which results in improved efficiency of operation of an electrolytic cell.

A further object of this invention is to provide a cell bath which reaches its maximum efficiency more rapidly.

In accordance with this invention, vanadium is added as a component of the cell feed material (about 95% MgCl₂·2H₂O) in amounts ranging from about 5 to 300 parts per million (p.p.m.), with a preferred range of from about 25 to 175 parts per million, based on the total weight of the feed.

The invention will better be understood when interpreted in accordance with the following examples in which the difference in efficiency, expressed in percent, is

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shown as the actual difference in operating efficiency between the control cell and the cell wherein vanadium is added to the cell feed. For example, if the efficiency of the control cell is 50% and the efficiency of the cell with added vanadium is 62%, the "difference" reported is +12%.

EXAMPLE 1

In a magnesium production plant, vanadium (as V₂O₅) was added to the feed of one circuit, while the other circuit (run at the same electrical conditions) was used as a control with no vanadium added. In order to negate any effect of a particular circuit, the control and test circuits were interchanged on different runs. The following table records the length of each run, the amount of vanadium added, the actual difference in current efficiency from that of the control circuit and a corrected difference. The correction was necessary because of a difference in the type graphite used in the cells of one circuit. This particular graphite consistently gave current efficiencies of about 0.4% less in those cells in which it was used. Thus, a positive or negative correction was necessary depending upon which circuit contained the V₂O₅ additive. The amount of V₂O₅ added is expressed as parts vanadium per million parts of feed by weight.

Run (days)	Vanadium (as V ₂ O ₅) added to feed, p.p.m.	Current efficiency difference	
		Actual, percent	Corrected, percent
73.....	15	0.6	+1.0
33.....	15	1.3	+0.9
18.....	7.5	1.5	+1.1
38.....	3.0	0.4	0

EXAMPLE 2

During a 30-day period 15 p.p.m. by weight vanadium (as V₂O₅) was added to the feed to all cells of a given circuit. Addition of vanadium was stopped and after one week, during which the efficiency gradually decreased as the vanadium content of the bath was depleted, the efficiency was again measured. The current efficiency for the 8th through the 17th day after the addition was stopped, averaged 3.5% less than during the time the V₂O₅ was being added to the feed.

EXAMPLE 3

To the feed of a single cell, which had been on stream for seven months and had been operating at a high level of efficiency for a three week period, was added 75 p.p.m. vanadium (as V₂O₅) based on the weight of feed. The addition was made on a continuing basis for 3 weeks and it was shown that the average current efficiency of the cell for the three week period during which the addition of vanadium had been made was 4.7% better than the average of the preceding three week period during which no vanadium had been added.

EXAMPLE 4

To the feed of a single cell just placed on stream was added 75 p.p.m. vanadium (as V₂O₅), based on the weight of feed, on a continuing basis. The start-up efficiency was compared with the average of 17 individual cells over a like start-up period to which no vanadium had been added. The efficiency of the cell containing the vanadium started higher and reached a higher level of efficiency faster than the average of the 17 cells without vanadium. The following tabular data shows the dif-

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ference in efficiency as measured over a 30-day period following start-up.

Time after starting cells:	Difference from control cells, percent
End 1st 5 days	+18.2
End 2nd 5 days	+15.8
End 3rd 5 days	+12.8
End 4th 5 days	+9.7
End 5th 5 days	+6.9

EXAMPLE 5

In an experimental set-up two cells were run under the same conditions and using the same bath compositions. To the feed of one cell was added vanadium as V_2O_5 , the other was maintained as a control. Efficiency was measured for each cell over a 5-day period. The difference in the average efficiencies are shown for different additions of vanadium in the table below:

Vanadium added (as V_2O_5) p.p.m. by weight:	Difference from control (percent cell efficiency)
(a) 56	+4.4
(b) 112	+6.1
(c) 168	+7.0

In all of the preceding examples the composition of the bath had a density greater than that of the magnesium metal recovered and thus the metal rises to the top of the cell bath. However, limited laboratory tests also indicate that this invention is useful with cell baths wherein the magnesium drops to the bottom of the cell, i.e. where the metal is heavier than the electrolyte. Examples of such cell baths are taught in U.S. Pat. No. 2,950,236 to L. G. Dean et al. The preferred range of composition for such a bath is as follows:

	Percent by weight
MgCl ₂	7-25
KCl	5-20
LiCl	70-87
CaF ₂	1.0

In U.S. Pat. No. 2,888,389, to E. J. Williams et al., another bath composition is disclosed in which the electrolyte is lighter than the magnesium. A preferred composition disclosed therein consists of 5-38% MgCl₂, 0.25-0.75% CaF₂, with the balance being entirely LiCl.

While it appears that the addition of vanadium in the cell feed in amounts of up to about 300 parts per million by weight or more improves the cell efficiency, adding vanadium in excess of this amount becomes unec-

nomical. Further, as stated before, the addition of less than 5 parts per million of vanadium to the cell feed appears to have little or no beneficial effect on the operating efficiency of the cell.

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While the addition of the vanadium has been described in connection with the amount supplied in the cell feed, vanadium could be supplied to the electrolyte directly in amounts which correspond with the previously stated ratios with respect to the amount of cell feed. The practical and preferred method of addition, however, is to the cell feed.

It has been found necessary to make the addition of vanadium on a continuous or repetitive basis, since analysis shows that most of the vanadium eventually is found in the sludge of the cell bath and in the exit gases.

Vanadium is conveniently added as vanadium pentoxide. However, other vanadium compounds which have the same or less volatility as V_2O_5 at the operating temperatures encountered (660-900° C.) in electrolytic cells used in producing magnesium metal may be used. Alternatively the vanadium may be added as a component of the graphite anodes used in the cell.

What is claimed is:

1. In the method of producing magnesium metal electrolytically, employing a graphite anode submerged in a molten electrolyte, by electrolyzing magnesium chloride in a molten salt bath at a temperature between about 660° C. and about 900° C., the improvement comprising adding vanadium to said molten salt bath wherein the amount added is from about 5 to about 300 parts by weight per million parts of feed material.

2. A method in accordance with claim 1, wherein said vanadium is added to said molten salt bath in an amount equal to from about 25 to about 175 parts per million by weight of said feed material.

3. A method in accordance with claim 1, wherein said vanadium is added as vanadium pentoxide.

4. A method in accordance with claim 1, wherein said molten salt bath is lighter than magnesium.

5. A method in accordance with claim 1, wherein said vanadium is a component of the cell feed material which is added to said molten salt bath.

6. A method in accordance with claim 1, wherein said molten salt bath comprises from 0-60% sodium chloride, 1-23% magnesium chloride, 0-23% calcium chloride, 0-20% barium chloride, 0-80% potassium chloride, 0-2% calcium fluoride, and trace amounts of other metal salts.

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