

Oct. 20, 1970

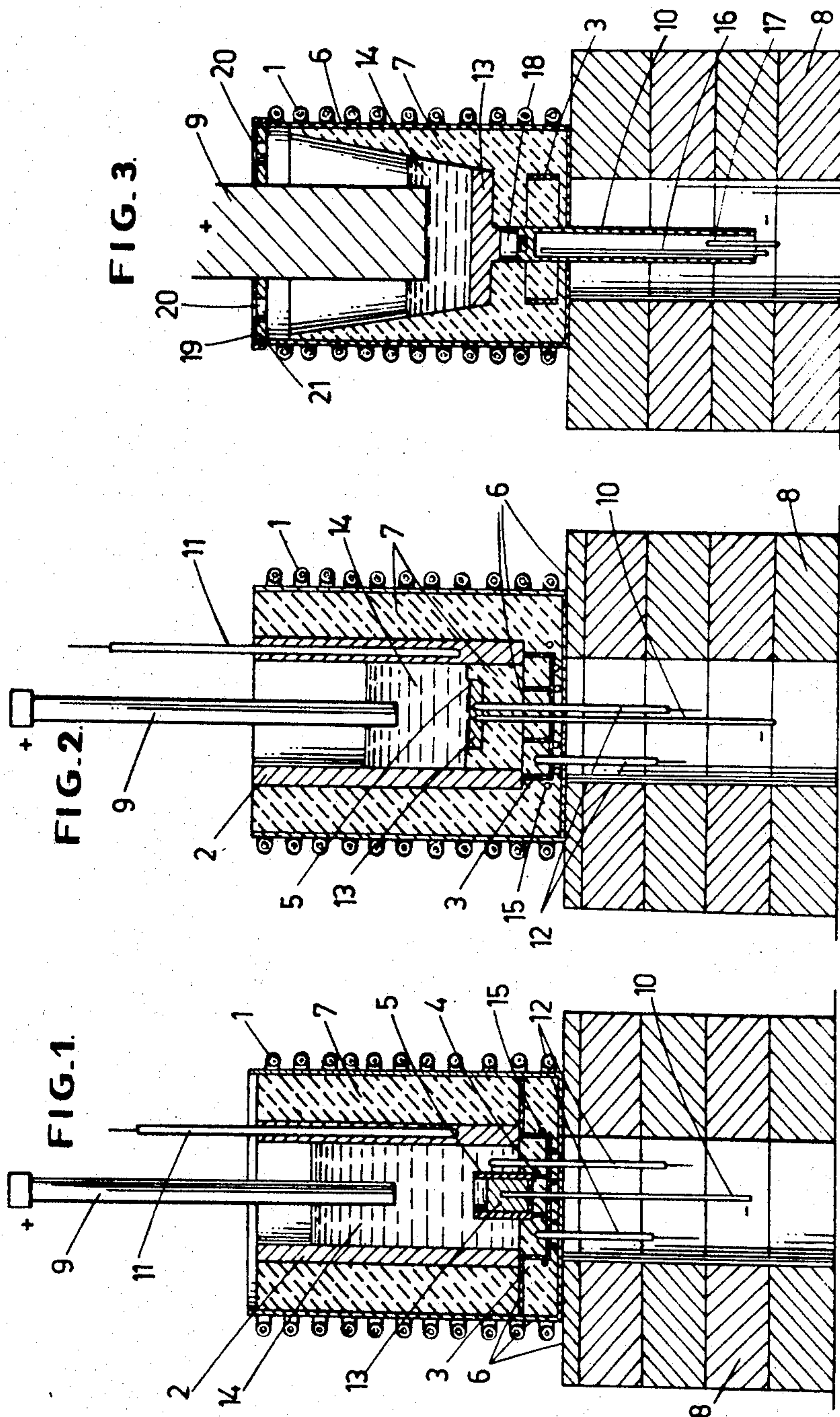
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3,535,214

PROCESS AND CELL FOR THE PRODUCTION OF MANGANESE OF LOW
CARBON CONTENT BY MEANS OF A FUSED ELECTROLYTIC BATH

Filed July 11, 1966

4 Sheets-Sheet 1



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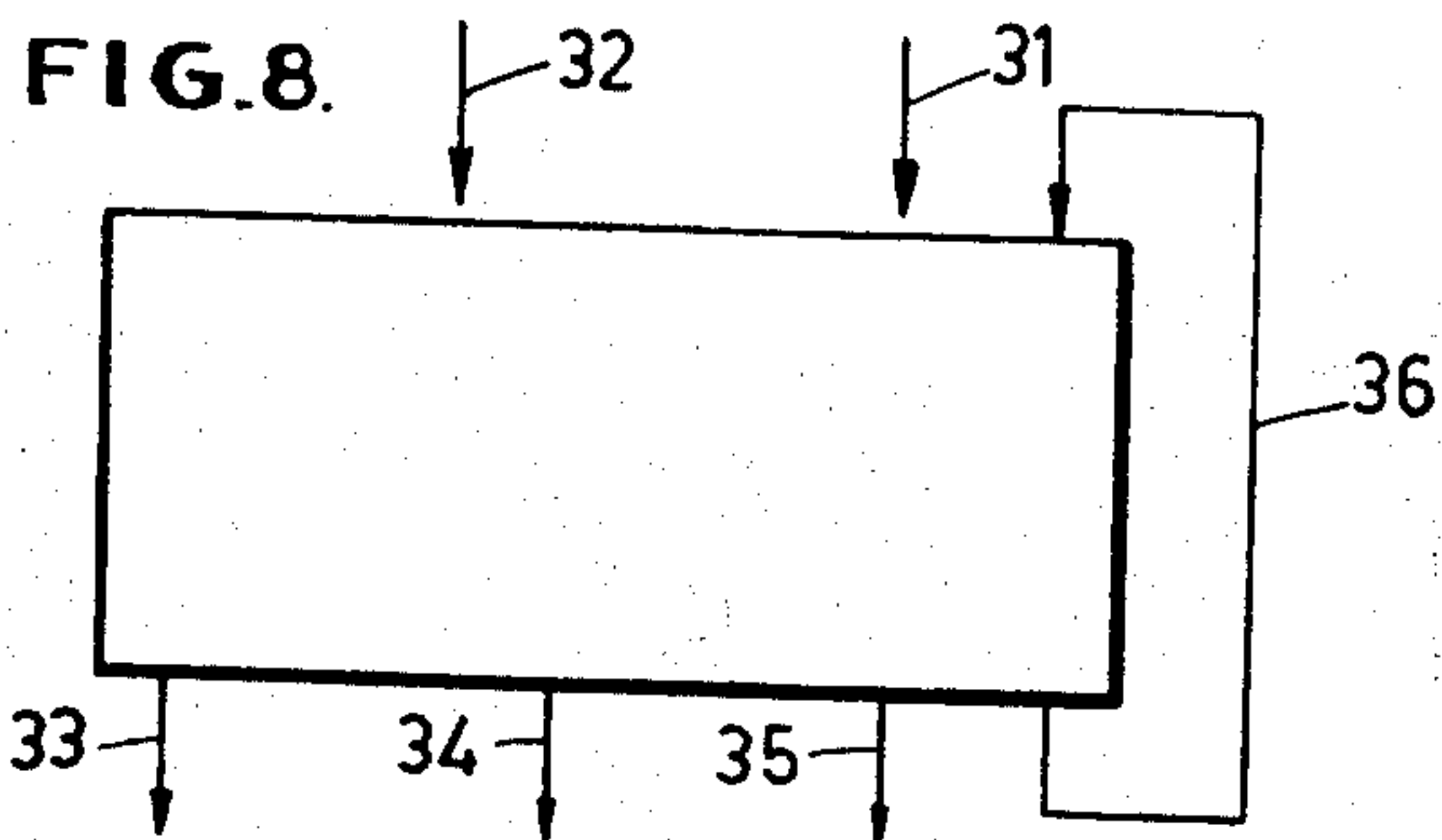
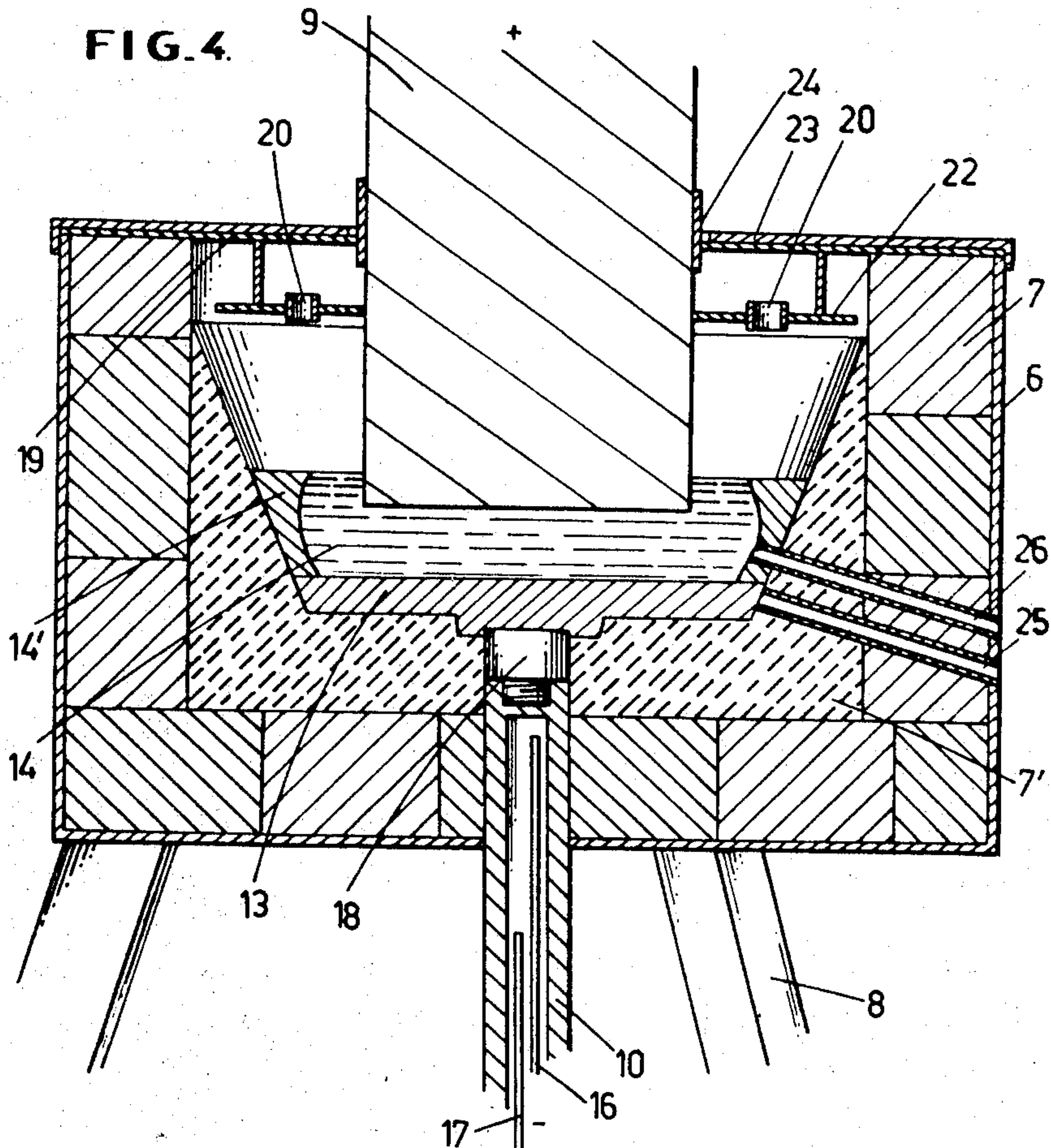
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Filed July 11, 1966

4 Sheets-Sheet 2



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Oct. 20, 1970

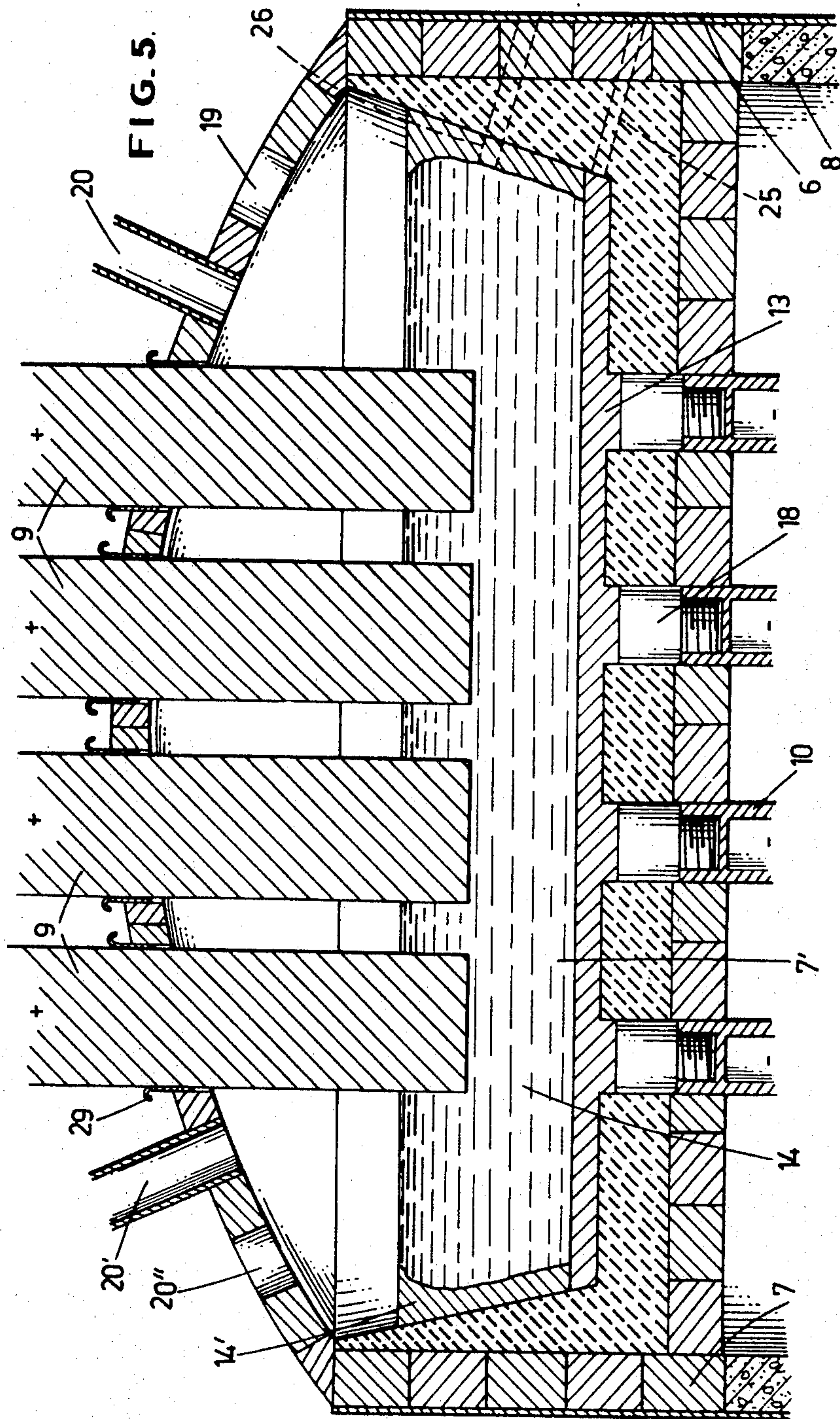
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Filed July 11, 1966

4 Sheets-Sheet 3



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Oct. 20, 1970

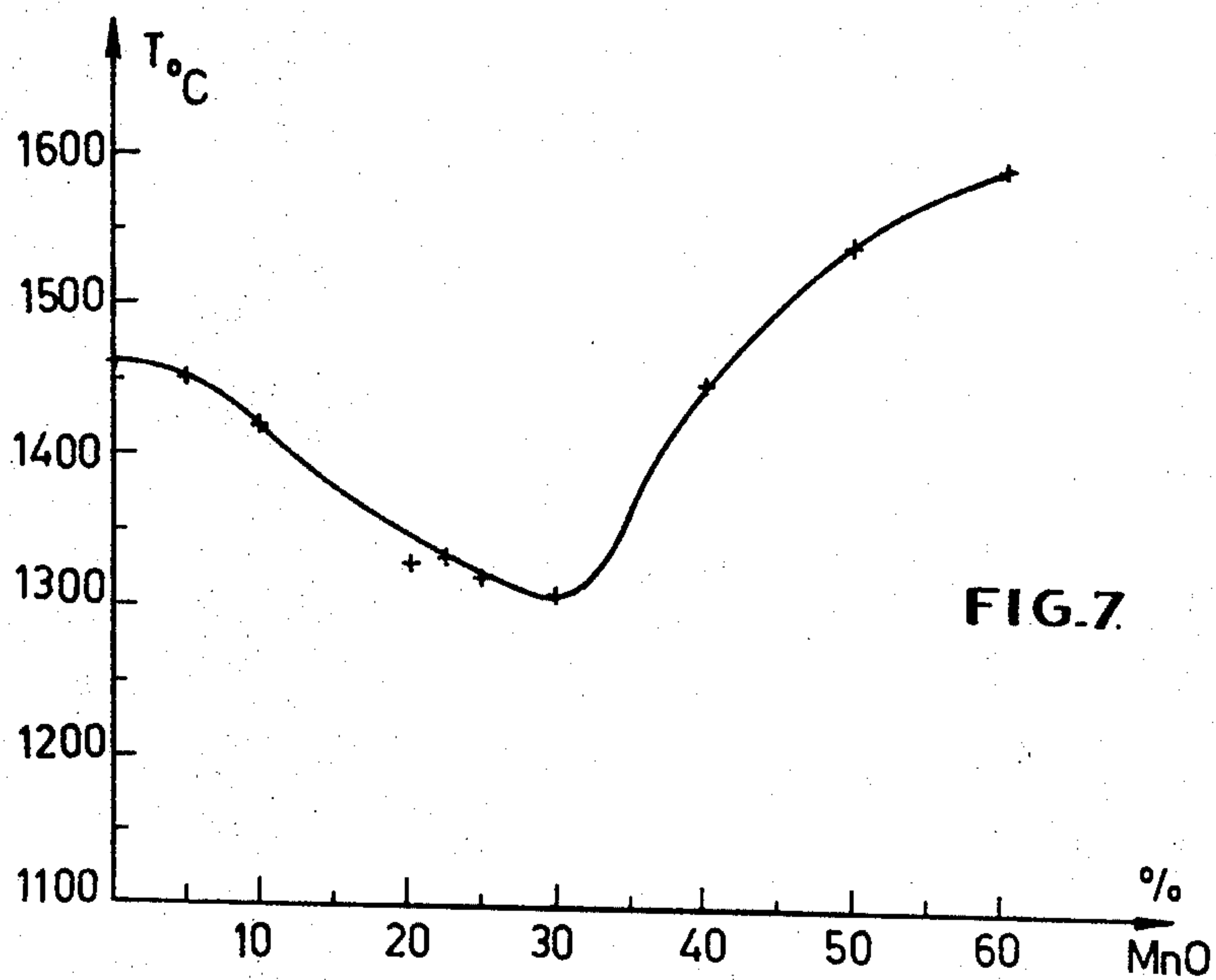
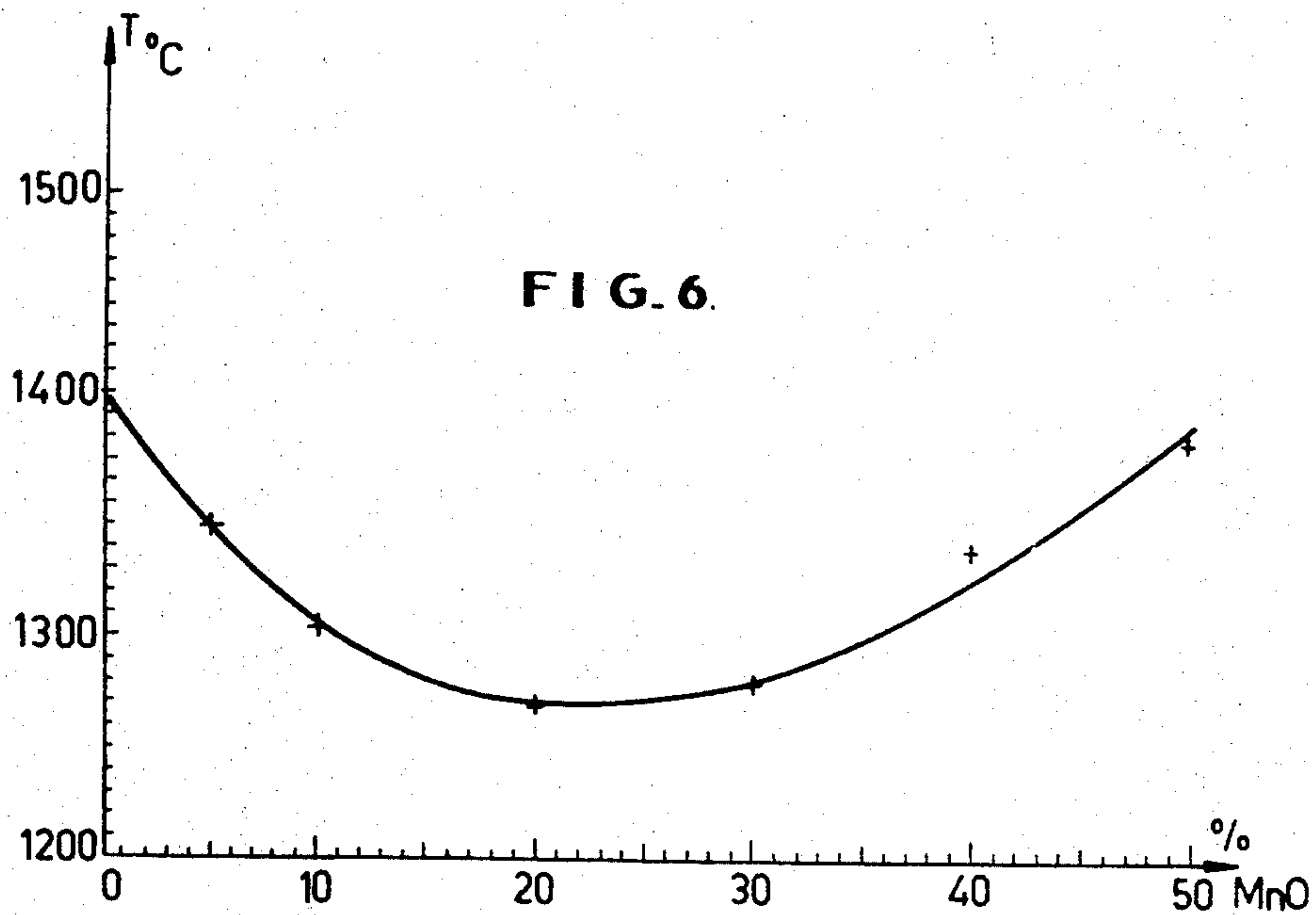
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Filed July 11, 1966

4 Sheets-Sheet 4



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3,535,214
**PROCESS AND CELL FOR THE PRODUCTION OF
MANGANESE OF LOW CARBON CONTENT BY
MEANS OF A FUSED ELECTROLYTIC BATH**
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Filed July 11, 1966, Ser. No. 564,301
Claims priority, application Belgium, July 16, 1965,
667,030; July 5, 1966, 683,660
Int. Cl. C22d 3/00

U.S. Cl. 204—64

6 Claims 10

ABSTRACT OF THE DISCLOSURE

Manganese is produced by electrolysis of a fused salt bath based upon a system such as $\text{MnO—SiO}_2\text{—CaO}$, $\text{MnO—SiO}_2\text{—MgO}$, MnO—CaO—MgO ,



and $\text{MnO—MgO—Al}_2\text{O}_3$, and complex systems based thereon, having a melting point less than 1500°C . In any such system, it is desirable that the ratio by weight of CaO or CaO+MgO to SiO_2 be not less than 0.75.

The present invention relates to a process for the production of manganese of low carbon content by means of a fused electrolytic bath.

According to U.S. Pat. 3,018,233, it is known to produce manganese by means of a fused electrolytic bath of molten mixtures containing a large quantity of calcium fluoride (50 through 80%) and manganese in the form of monoxide.

However, the presence of fluorides in the electrolyte gives rise to serious disadvantages. Indeed there is practically no refractory material of economic application able to resist the electrolyte for a sufficient length of time and act as a crucible, as carbon cannot be taken into consideration as it carburizes the manganese produced. A certain volatilisation of fluorides always takes place at the high temperatures at which the electrolysis has to be carried out, these temperatures being higher than the melting temperature of manganese and generally of the order of $1,350^\circ\text{C}$. This necessitates the provision of a very expensive installation for the gas purification in order to avoid as far as possible to contaminate the surrounding countryside. Moreover, there is a considerable risk of deteriorating all the parts of the furnace which would be fabricated from silica. Similarly, if the furnace considered is fed with an ore or a slag containing for example silica, a reaction may take place between the calcium fluoride and the silica to form volatile silicon tetrafluoride, the latter, being liable to condense in the gas purification pipes, risks therefore to clog the latter. If, on the other hand, the dew point was then reached in these pipes, hydrofluosilicic acid might be formed so that there would be a risk of entailing a fast corrosion of the pipes considered. Moreover, should the charge or the furnace atmosphere be slightly damp, the formation of gaseous hydrofluoric acid may be expected, with the serious consequences resulting therefrom. Lastly, when the furnace is not fed with pure manganese monoxide, the constituents of the gangue progressively dilute the electrolyte, so that the latter's concentration in calcium fluoride becoming inadequate and the volume of material present in the furnace growing all the time, it becomes necessary to throw out periodically a part of the electrolyte, which constitutes a loss of calcium fluoride a fairly expensive product.

The object of the present invention comprises essentially to overcome the said disadvantages and to provide

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a process for the production of metallic manganese by means of a fused electrolytic bath, on an industrial scale, the starting material being an electrolyte of well specified composition so as to produce an industrially pure manganese at a very interesting cost price.

For that purpose, the process according to the invention comprises the use of an electrolytic bath selected among the group comprising the ternary systems



and $\text{MnO—MgO—Al}_2\text{O}_3$ as well as the complex systems based on compounds of said ternary systems.

Indeed, it has been noted that in a rather unexpected manner, it is possible to produce easily and economically manganese by means of an electrolytic bath with a composition in accordance with the formulation given above.

The ternary diagram of the MnO—CaO—SiO_2 system, for example, drawn up by Glasser (J. Am. Cer. Soc. 243 (1961)45) clearly shows a large range of compression for which the melting temperature remains below $1,350^\circ\text{C}$. In any case, and although the theoretical temperature of inversion of the deoxidation reaction of MnO by the anodic carbon with formation of CO is about $1,325^\circ\text{C}$., experience shows, in a rather unexpected manner, that even at $1,600^\circ\text{C}$., the kinetics of this thermal reduction is far lower than that of the electrochemical reduction. It follows therefrom that the electrolysis of said bath may very well take place for example at $1,500^\circ\text{C}$. without there being an exaggerated contamination of the manganese deposited on the cathode by the carbon. The range of composition suitable for the electrolysis under consideration is therefore very large.

However, in order to limit the silicon content in the manganese deposited on the cathode while exhausting sufficiently the electrolytic bath of manganese, according to an advantageous form of embodiment of the object of the invention, the process comprises adjusting the quantity of lime with reference to the quantity of silica in the electrolytic bath in a ratio by weight which shall not be less than .75.

According to a particularly advantageous form of embodiment of the object of the invention, the process comprises adjusting the total of the quantity of lime and magnesia with reference to the total of the quantity of silica and alumina in the electrolytic bath in a ratio by weight which shall not be less than .75.

According to a preferred form of embodiment of the object of the invention, when use is made of a carbonate ore said ore is decarbonated, prior to the electrolysis thereof in a nonoxidising atmosphere.

The process according to the invention may advantageously be also used to prepare a manganese based alloy.

For that purpose, at least one metal having an affinity for oxygen less than, equal to, or slightly in excess of that of manganese is introduced in the electrolytic bath so that said metal or metals are deposited at the cathode alongside of the manganese, so as to alloy itself with the latter. In the case where the affinity of said metal for oxygen is in excess of that of manganese, it will be sufficient to maintain a cathodic current density sufficiently high or to exhaust the bath partially of manganese in order to achieve this. Or again, if the melting temperature of the added metal is lower than the temperature of the electrolyte and of the melted cathodic metal, it is possible to introduce it directly in metallic form in the electrolysis cell.

The invention also relates to an electrolysis cell which may, in particular, be used for working the said process.

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Said cell comprises a container above which is mounted at least one carbon anode and the bottom thereof is provided with a cavity wherein terminates one lead of cathodic current, said cavity being intended to contain metal, such as manganese, to be extracted, providing the cathode, an electrolyte being located above the latter and comprising said metal in the shape of an oxide compound, characterized in that the lead of cathodic current is effected by means of a refrigerated conductor so that it shall be coated with a protective layer of said solidified metal, a liquid layer of the said metal floating on top of the solidified metal.

Other details and features of the invention will become apparent from the description of the accompanying drawings, by way of nonlimitative example, of several forms of embodiment of the process according to the invention and of cells which may, in particular, be used for working said process.

FIG. 1 is an elevational view, partially broken away, of a first form of embodiment of the object of the invention.

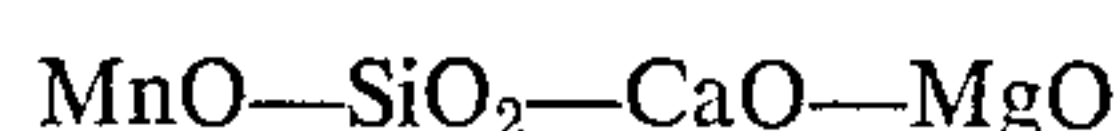
FIG. 2 is an elevational view, partially broken away, of a second form of embodiment of the object of the invention.

FIG. 3 is an elevational view, partially broken away, of a third form of embodiment of the object of the invention.

FIG. 4 is an elevational view, partially broken away, of a fourth form of embodiment of the object of the invention.

FIG. 5 is an elevational view, partially broken away, of a fifth form of embodiment of the object of the invention.

FIG. 6 shows a section in the liquidus of the



system plotted over the quantity of MnO.

FIG. 7 shows a section in the liquidus of the



system plotted over the MnO content.

FIG. 8 is a diagrammatic view illustrating the process according to the invention.

In the different figures, the same reference numerals designate similar elements.

FIG. 1 shows a laboratory cell used to demonstrate that it is possible to produce by the electrolysis of certain electrolyte compositions manganese with a very low carbon concentration. This cell comprises essentially an induction coil 1 of 18 turns cooled by a water circulation and supplied in a medium frequency (8,000 Hz.) by an alternator not shown in the figure, the interior sidewall of the cell being provided by an inner graphite casing 2 intended to contain the electrolyte, a crucible support 3, made from copper sheet cooled by a water circulation, a graphite crucible 4 protecting against attack by the molten electrolyte an alumina crucible 5, with a bored bottom intended to receive the manganese 13 providing the cathode, asbestos sheets 6 insulating the different parts of the cell the ones from the others, a wall and a bottom of carbon free refractory material 7, for example made from tamped magnesia, a cell support 8 made from refractory bricks, a graphite anode 9, a cathodic current lead 10 made from tungsten, a thermocouple 11 made from PtRh 18 and two other thermocouples 12 made from chromel-alumel. The electrolyte 14 is therefore placed in the graphite casing 2, on the magnesia hearth 7, in contacting relationship, on the one hand with the cathodic manganese 13, and on the other hand, with the anode 9.

FIG. 2 shows another laboratory cell used for the run of tests having for their object to determine the conditions under which it is possible to produce manganese having a low silicon content while exhausting the electro-

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lyte as much as possible. Said cell comprises same as that shown in FIG. 1 an induction coil 1, a graphite casing 2, a crucible support 3 made from copper sheet cooled by water flowing in the pipes 15, asbestos sheets 6, a wall and a hearth made from refractory material 7, such as carbon free tamped magnesia, a support 8 made from refractory bricks, a graphite anode 9, a cathodic current lead 10 made from tungsten, a thermocouple 11 made from PtRh 18 and two other thermocouples 12 made from chromel-alumel. The essential difference between the cells shown in FIG. 1 and in FIG. 2 is the fact that the crucible 5 of the cell shown in FIG. 1 is replaced by a cylindrical recess 5 provided in the hearth of the cell. As in the cell shown in FIG. 1 the electrolyte 14 is placed in the graphite casing 2, on the magnesia hearth 7, in contacting relationship with the cathodic manganese 13 and with the anode 9.

The FIG. 3 shows a third form of embodiment of a laboratory cell, which was also used in the run of the orientation tests and which differs essentially from the cells shown in the FIGS 1 and 2 on account of the fact that it does not comprise a graphite casing permitting to provide a supplementary heating on account of the medium frequency induction in said casing. Said cell comprises essentially a coil 1, wherein flows cooling water and which surrounds a wall 6 made from copper sheet, an interior wall 7 of carbon free magnesia based refractory concrete, a crucible support 3 made from copper sheet, a cell support 8 carried out in refractory bricks, a cathodic current lead comprising a copper tube 10 and cooled internally by a water flow admitted through a pipe 16 and leaving by a pipe 17 of said tube 10, a mild or stainless steel component 18 being screwed on the top end of the pipe 10. This cell also comprises liquid manganese 13 providing the cathode, an anode 9, electrolyte 14 in contacting relationship with said anode and said cathode as well as a lid 19 provided with bores 20 and protected in its bottom portion by an asbestos screen 21. Said lid 19 is used to maintain, inside the cell, a reducing atmosphere in order to prevent a repeated oxidation of the manganese monoxide of the charge, while the bores 20 are used for the progressive charging of said cell.

FIG. 4 shows an electrolysis cell which was used to carry out large scale laboratory tests. In principle, it corresponds fairly well to the cell shown in FIG. 3. It comprises an outer casing 6 made from ordinary steel sheet carried on a tripod 8, a wall and a bottom made from refractory bricks 7, a carbon free magnesia concrete refractory lining 7', provided inside the wall and the bottom 7, a cathodic current lead comprising a copper tube 10 internally cooled by a circulation of water supplied through a pipe 16 and withdrawn through a pipe 17, a mild or stainless steel component 18 being screwed in the top end of the copper tube 10, a bath of liquid manganese 13 providing the cathode, a graphite anode 9, a stainless steel thermal screen 22 provided with bores 20 for the progressive charging of the cell, three angles 23 mounted radially and carrying, on the one hand, the screen 22 and, on the other hand, a tubular sleeve 24 guiding the anode 9, removable steel lids 19 protected on their inside faces by a layer of asbestos. Said lids are partially supported by the angles 23 and are used to maintain a reducing atmosphere in the cell in order to prevent the repeated oxidization of the manganese monoxide.

Said cell also comprises an electrolyte 14 in contacting relationship with cathodic manganese 13 placed in the bottom of the cell. When the cell is in normal operation, it is possible to maintain a layer of solid electrolyte 14' in contacting relationship with the lining 7'. It is, however, sufficient to increase the power slightly in order to melt the electrolyte charge completely. Lastly, a tap hole 25 is provided for the metal 13 and another hole 26, provided above the first tap hole 25 is provided to remove exhausted electrolyte.

FIG. 5 shows an electrolysis cell which could be used on an industrial scale. It comprises an outer casing 6 made from ordinary steel sheet carried on a support 8 carried out, for example, in the shape of concrete pillars, walls and a bottom made from refractory bricks 7, a carbon free magnesia concrete inside lining 7', cathodic current leads comprising copper tubes 10 at the top of each of which is provided a mild or stainless steel component 18 screwed on the top ends of said tubes 10, the latter being cooled internally by a water circulation, a bath of liquid manganese 13 providing the cathode, a plurality of anodes 9 made from, for example Söderberg quality, carbon, a vault 19 made from silica provided with bores 20 connected to pipes, not shown in the figure, in order to exhaust the gases released at the anode, bores 20' connected to feed hoppers, also not shown in the figure, and lastly bores 20'' closed by a door in order to permit watching the run of the cell and the descent of the charge. The electrolyte 14 is contained in the cell and is in contacting relationship with the cathodic manganese 13 and the anodes 9. When the cell is in normal operation, it may be of advantage to maintain a layer of solid electrolyte 14' on the surface of the lining 7'. Lastly, a tap hole 25 enables the removal of the metal built up on the cathode while another hole 26 is used to remove exhausted electrolyte. Where the anodes 9 pass through the vault 19, the leak tightness is provided by means of an appropriate device 29. The vault 19 maintains a reducing atmosphere inside the furnace in order to prevent the repeated oxidization of the manganese monoxide. However, in certain cases where a slight repeated oxidization of the manganese monoxide is permissible, said vault need not be provided.

Hereafter are given some examples of tests illustrating the process according to the invention.

FIRST TEST

The cell used for this test is shown in FIG. 1. 100 gr. of electrolytic manganese were provided prior to the electrolysis, in the alumina crucible 5, in order to provide an adequate cathodic surface after melting. 2 kgs. of a mixture containing 45% MnO, 37.5% SiO₂ and 17.5% CaO by weight were then introduced in the cell. The melting of the charge was carried out by medium frequency heating. 30 minutes after stabilization at about 1,400° C. of the temperature recorded by the thermocouple 11, the anode was introduced in the electrolyte 14 formed by said mixture and the electrolysis current was cut in. This test was carried out with current intensities between 80 and 150 amps. and electricity quantities from 50 through 200 amps.-hr. The noted cathodic current efficiencies, based on the bivalent manganese, varied between 35 and 65%. The test considered was carried out for three different systems of anodic operation. In the arc system, the voltage at the cell terminals was between the limits of 35 and 60 v. for 100 amps. The carbon content achieved in this case was far below 0.01%. In the anode effect system, i.e., when the latter is dipped but not wetted by the electrolyte, the voltage at the cell terminals was about 20 v. for 100 amps. The carbon content being .07% on the average. Lastly, in the case of the test carried out with the anode dipped and wetted by the electrolyte, the voltage at the terminals was close on 10 v. for 100 amps. and the carbon content was between the limits of 0.04 and 0.09%.

SECOND TEST

The cell used to carry out this test is shown in FIG. 2.

Before the electrolysis, 100 gr. of electrolytic manganese were provided in the cavity 5 of the cell hearth, in order to provide an adequate cathodic surface after melting. Thereafter, a charge of a decarbonated ore was introduced in the cell. The analysis of said ore was as follows:

	Percent
MnO -----	56.5
Co ₂ -----	0.4
CaO -----	7.85
MgO -----	3.63
Al ₂ O ₃ -----	2.76
SiO ₂ -----	19.77
Fe -----	3.30
Mn ₃ O ₄ -----	traces.

By means of an addition of lime and silica, the MnO content was brought down to 46% and the ratio by weight of the total of the quantity of lime and magnesia with reference to the total of the quantity of silica and alumina was adjusted to a value of .85. The total quantity of the charge used was 2 kgs.

Melting was carried out using a medium frequency heating, the electrolysis starting 15 minutes after the temperature recorded by the thermocouple 12 penetrating the cathodic metal 13 exceeded 1,250° C.

For a temperature of 1,450° C. recorded by the thermocouple 11, a current intensity of 150 amps. and a quantity of electricity of 900 amps.-hr., the average voltage at the cell terminals was about 8.3 v. The cathodic current efficiency, based on the valence 2 for manganese, was about 70% which corresponds to a rate of exhaustion of the electrolyte of 92%. The silicon content of the metal produced was 2%. The carbon content was, however, very high (2.8%) on account of the fact that the cathodic metal had come into contacting relationship with the graphite casing 2.

THIRD TEST

The cell used for this test is shown in FIG. 3.

Prior to electrolysis, 500 gr. of electrolytic manganese were provided in the bottom of the crucible made from refractory concrete. An arc was establishing between the graphite anode 9 and the manganese 13. Thereafter a charge comprising 3.4 kgs. of a mixture made up of 35% of MnO, 34% of CaO and 31% of Al₂O₃ by weight was immediately but gradually introduced in the cell. From the moment when the charge was completely melted, a temperature of about 1,650 to 1,700° C. measured with a radiation pyrometer was maintained in the cell. The electrolysis was carried out by anodic effect system at about 20 v. and 500 amps. After passing 900 amps.-hr. through the cell the anode was lifted and the whole was left to cool.

It proved impossible to evaluate a correct current efficiency on account of the excessive volatilisation of the starting manganese during the arc priming.

The analysis of the metal produced was as follows:

	Percent
C -----	2.46
Al -----	2.44
Ca -----	.04

The high carbon content originates from the frequent short circuits between the carbon anode and the cathodic manganese during the melting period of the electrolyte. As regards the aluminum and calcium content this must be ascribed to the excessive cathodic current density.

A modification of this test comprised lowering the anode 9 in the electrolyte 14 so as to escape the anode effect. A voltage of 19 v. for 700 amps. was noted for a distance of 3.5 cm. between anode and cathode.

FOURTH TEST

The cell used to carry out this test is shown in FIG. 4.

Before the electrolysis, 5.3 kg. of ferromanganese were provided on the cell hearth, said ferromanganese comprising 94% manganese, .09% carbon and 1.58% silicon, the remainder being mainly iron. An arc between the graphite anode 9 and the ferromanganese 13 was then established. Thereafter, a charge comprising 20 kgs. of a mixture of pyrolusite based and manganese carbonate

ores was immediately, but gradually introduced in the cell. This mixture had been reduced and adjusted beforehand so as to achieve a content of 44% by weight of MnO and a ratio by weight

$$\frac{CaO+MgO}{SiO_2+Al_2O_3}$$

of the charge was as follows:

	Percent
MnO -----	44
SiO ₂ -----	24
Al ₂ O ₃ -----	2
MgO -----	7
CaO -----	19
FeO -----	4

As soon as the charge melted, a temperature within the limits of 1,420 and 1,500° C. measured by means of a vanishing filament optical pyrometer was maintained in the electrolyte 14. The average current intensity was 1,200 amps. for a terminal voltage of 15 v., while the distance between the anode 9 and the cathode 13 exceeded 5 cm. these conditions being maintained for 5 hours. After 5 hours the anode 9 was withdrawn from the electrolyte 14 and the cell was left to cool slowly. After about 24 hours of stoppage of the cell, the exhausted electrolyte and the metal produced were withdrawn, said electrolyte still containing 2.1% of MnO and substantially no more iron, the quantity of metal being 9.5 kgs. and meeting the following average analysis:

	Percent
Mn -----	88
Si -----	1.60
C -----	.06
Fe -----	10.25

The cathodic current efficiency was about 70%.
A loss of manganese with reference to the total quantity introduced in the cell was due on the one hand to the volatilisation in the arc of a part of the metal initially provided on the cell hearth and, on the other hand, to the fact that part of the electrolyte remained solid in contacting relationship with the side walls of the cell and therefore did not participate in the electrolysis. The noted current efficiency was therefore under evaluated for the same reasons.
The current intensity used for this test corresponded to an average current density of about 350 amps./dm.². The average carbon content of the final metal produced was less than .06%.

FIFTH TEST

The cell used to carry out this test is shown in FIG. 4. A mixture of 35 kgs. of ores reduced beforehand down to MnO and adjusted was prepared so as to achieve a MnO content of 50% by weight and a ratio by weight:

$$\frac{CaO+MgO}{SiO_2+Al_2O_3}$$

having a value of .82. The average composition of the charge was as follows:

	Percent
MnO -----	50
FeO -----	2.5
Al ₂ O ₃ -----	4.9
SiO ₂ -----	21.1
MgO -----	8.5
CaO -----	12.8

Beforehand this ore was subjected to an electrolytic removal of the iron. For that purpose, 5.7 kgs. of ferromanganese, the analysis of which is given in the fourth test, were provided on the cell hearth. An arc was thereafter established between the graphite anode 9 and the

ferromanganese, the said charge of ores being thereupon immediately, but progressively, introduced in the cell.

As soon as the charge was completely melted, the electrolyte was maintained at a temperature within the limits of 1,380 and 1,500° C., a regular check of the iron content of the electrolyte being carried out by means of X-ray fluorescence analysis. The current intensity was maintained at 1,100 amps. for 10 v. the distance between the anode and the cathode being kept between 6 and 8 cm. These conditions were maintained for 4 hours, until the iron content of the electrolyte had dropped below .2%. At that moment the anode was removed from the bath and the cell was left to cool. About 24 hours after the stoppage of the cell, the ironfree electrolyte still containing about 40% MnO as well as 8.9 kgs. of metal was withdrawn. The analysis of this metal with reference to the metal actually produced by the electrolysis yielded approximately the following composition:

	Percent
Mn -----	49.6
Fe -----	49.8
Si -----	.4
C -----	.04

The cathodic current efficiency, under evaluated for the same reasons as for the fourth test amounted to 73%.

In the following stage, 27 kgs. of ironfree electrolyte with 40% MnO originating from the previous operation were taken up again and subjected to an exhaustion electrolysis in order to produce a manganese with a low iron content.

For that purpose, 5 kgs. of electrolytic manganese of 99.9% manganese were provided on the cell hearth and an arc established between the graphite anode 9 and said manganese. Immediately afterwards, ironfree electrolyte coarsely crushed so as to pass a 1-inch sieve was gradually introduced in the cell.

As soon as the charge of electrolyte was completely melted, a temperature between the limits of 1,300 and 1,450° C., was maintained therein, the current intensity being about 1,050 amps. with a terminal voltage of 10 v., the distance between the anode and the cathode being 5 cms. These conditions of electrolysis were maintained for 8 hours, until the MnO content of the electrolyte determined by X-ray fluorescence had dropped to 13%. At that moment the anode was withdrawn from the bath and the whole was left to cool. About 24 hours after the stoppage of the cell, the electrolyte exhausted down to 13% of MnO and 10.8 kgs. of metal were withdrawn from the cell. The analysis of said metal, with reference to the metal actually produced by the electrolysis, yielded an average composition as follows:

	Percent
Mn -----	96.0
Fe -----	2.35
Si -----	1.56
C -----	.04

The cathodic current efficiency, under evaluated as mentioned for the fourth test was 69%.

It should be noted, as follows moreover from what has been stated hereinbefore, that the cathodic liquid manganese is carried on a solid layer formed by one or more refractory oxides which do not react with the manganese. The electric cathodic contact between the liquid manganese and the feed of cathodic current is effected by means of a conductor, which is cooled so as to become coated with a layer of solidified manganese. The reasons for this is to prevent any contamination of the manganese produced at the cathode by the metal or metals comprising the cathodic current feed. Although this is not absolutely essential, it may be of a practical interest for the electrolysis cell to be built with dimensions such that the liquid electrolyte is never

in immediate contacting relationship with the refractory walls and bottom but rather with a crust of solidified electrolyte. This precaution may indeed lead to a fairly important economy of refractory materials.

As follows from said tests, the electrolyte may comprise three or a plurality of the following compounds: MnO, CaO, SiO₂, Al₂O₃ and MgO. Thus in particular a mixture of oxides comprising 30% of CaO, 20% of MgO and 50% SiO₂ by weight may dissolve up to 60% of MnO by weight while maintaining all the time a melting temperature below 1,450° C., as shown in FIG. 6. A substantial lowering of the melting temperature is noted when 4% by weight of alumina is added to said mixture. Mixtures of this kind, when subjected to electrolysis, have revealed themselves even more interesting than the MnO-CaO-SiO₂ mixtures. Indeed, for anodic and cathodic current densities close to 250 amps./dm² and for distances between anode and cathode of not less than 5 cms., it is possible to maintain voltages at the cell terminals within the limits of 5 and 7 v., the temperature of the electrolyte not exceeding 1,450° C. Moreover, it is easy with these mixtures to achieve an index of basicity:

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$$

equal to or higher than unity, which insures a silicon content of less than one or two percent for very low residual MnO contents in the electrolyte (less than 3%).

Of course, other oxides may still be present in the electrolyte as is the case, for example, when ores reduced beforehand or decarbonated are used as electrolyte. It is then sufficient to adjust the composition of the gangue in such a manner that it corresponds approximately to a mixture of oxides considered as particularly interesting as a solvent of MnO.

As regards the electrolyte built up from the three oxides MnO, CaO and Al₂O₃, this ternary system was investigated for a ratio by weight of CaO/Al₂O₃ of 1.1. FIG. 7 shows the melting temperatures of this mixture plotted over the MnO content. It should be noted that the melting temperature does not exceed 1,450° C. in so far as the quantity of MnO remains below 40%. It is possible to subject said mixture to the electrolysis at about 1,550 through 1,600° C., with a voltage at the cell terminals of less than 10 v. for an average current density of 250 amps. per dm.² and a distance between the anode and the cathode of 5 cms. In that case a metal of very high purity as regards the silicon content is produced.

Generally speaking the ranges of composition of electrolyte which appear to offer greatest interest for the performance in practice of the process according to the invention are the following:

In the case of electrolytes mainly based on the ternary system MnO-CaO-SiO₂:

MnO—less than 60%
CaO—25 through 55%
SiO₂—15 through 75%

The optimum range of concentration of the starting electrolyte in order to achieve a silicon content of less than 2% in the manganese produced with a sufficiently high range of exhaustion of the electrolyte is narrower and is substantially within the following limits:

MnO—2 through 45%
Ratio by weight CaO/SiO₂ higher than or equal to 0.75.

In the case of electrolytes mainly based on the

MnO-CaO-Al₂O₃

ternary system:

MnO—less than 40%
Ratio by weight CaO/Al₂O₃ from .72 through 1.24

In the case of electrolytes based on the

MnO-CaO-MgO-SiO₂-Al₂O₃

complex system:

MnO—less than 60%
Al₂O₃—0 through 60%
MgO—0 through 28%
CaO—25 through 55%
SiO₂—15 through 75%

The ranges of optimum compositions to be used in practice are conditioned, apart from the conditions of the said two ternary systems MnO-CaO-SiO₂ and MnO-CaO-Al₂O₃, on the one hand by the necessity to achieve a ratio by weight

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$$

having a value higher than .75 in so far as the silica is present in the electrolyte and that one wishes to achieve a manganese with a low silicon content, and on the other hand by the need to seek a composition of exhausted electrolyte the melting temperature of which shall still be less than 1,500° C. This has moreover been demonstrated by the Tests 4 and 5.

The anode used in the electrolysis cell for working the process according to the invention may be of amorphous carbon, of graphite or more currently of Söderberg type.

The tapping of the metal deposited on the cathode on the one hand, and of the exhausted electrolyte on the other hand, does not raise any special problems and is of current metallurgical practice.

The metal produced by electrolysis is essentially characterized by a very low carbon content (less than .1%) and a low silicon content (less than 2%). The content of other impurities is conditioned by the purity of the electrolyte. Thus all of the iron contained in the electrolyte passes into the manganese deposited at the cathode. The same would be the case for any other element having an affinity for oxygen lower than, equal to or slightly in excess of that of manganese, i.e., for example, chromium, cobalt, copper, nickel, silicon and aluminium. The silicon content of the metal produced at the cathode is essentially conditioned by the index of basicity of the electrolyte and of the degree of final exhaustion of the latter. If said index is maintained at a value equal to or higher than unity and the electrolysis is stopped at the time when about 15% MnO remain in the electrolyte, it is possible to achieve silicon contents of less than 1%. Under those conditions, and in so far as the electrolyte does not contain impurities more reducible than MnO, it is possible to produce a manganese of about 99% or more.

On the other hand, if a manganese with a higher silicon content is desired, it will be sufficient to maintain the index of basicity of the electrolyte sufficiently low, for example below .75 and to continue the electrolysis until a high rate of exhaustion of the electrolyte is reached.

In the case when a manganese ore or a mixture of ores thereof is used to make up the electrolyte, said ores may be subjected beforehand to a treatment of partial reduction or decarbonation, so that said manganese shall be present in the electrolyte as monoxide. It may also be necessary to add to said ore or mixture of ores the oxides needed in order that the overall composition of the electrolyte shall approximate the ideal composition mentioned hereinbefore.

In order that the material balance of an electrolysis cell working on an industrial scale according to the

process of the invention, be better appreciated a non limitative example is given hereinafter:

The ore used at the start shall meet, after reduction beforehand, the following average analysis:

	Percent
MnO -----	63
SiO ₂ -----	16.5
Al ₂ O ₃ -----	2.7
CaO -----	8.4
MgO -----	2.8
FeO -----	1.4

The remainder being alkaline oxides and alkaline earths and titanium oxide.

In order to adjust the ratio

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$$

of said ore to the value of .85, it is necessary to add 32.4 kgs. of lime for each 1,000 kgs. of ore reduced beforehand. In the case when the electrolyte may contain a maximum of 45% of MnO and a minimum of 15% MnO, it is necessary, for normal operation, in order to produce 1,000 kgs. of ferromanganese of 94% manganese, with less than .1% of carbon and less than 2% of silicon to introduce in the cell about 2,190 kgs. of ore reduced beforehand to 63% MnO and 71 kgs. of lime and to recycle about 1,142 kgs. of electrolyte exhausted to 15% of MnO. The latter electrolyte is merely kept in the electrolysis cell at the end of the cycle. It is therefore necessary to reject 939 kgs. of electrolyte exhaust to 15% MnO for every 1,000 kgs. of ferromanganese produced.

FIG. 8 is a diagrammatic illustration of said different operations.

The arrow 31 represents the addition of 2,190 kgs. of decarbonated ore with 63% MnO. The arrow 32 represents the addition of 71 kgs. of lime, the arrow 33 represents the withdrawal of 1,000 kgs. of ferromanganese with 94% manganese, less than .1% of carbon and less than 2% silicon. The arrow 34 represents the removal of 323 kgs. of oxygen combined with the carbon of the anode. The arrow 35 represents the removal of 939 kgs. of electrolyte exhausted down to 15% MnO. The arrow 36 represents a recycling of 1,142 kgs. of electrolyte exhausted down to 15% MnO.

In the present case the metallurgical efficiency of said operation would be 90%.

If the manganese ore mixture contains iron, it is possible to produce a manganese with a low iron content by carrying out beforehand an operation to remove the iron.

According to the invention, the ore is subjected to an electrolysis similar to that permitting to achieve a manganese with little impurities, without, however, proceeding as far as to exhaust the manganese from the electrolyte. It is thus possible to produce, on the one hand, an electrolyte containing 35% or more of MnO, for example, but the iron of which has been removed, which is afterwards subjected to an exhaustion electrolysis in another electrolysis cell of the type described hereinbefore and, on the other hand, a ferromanganese of low carbon and silicon content, having a high commercial value compared with heavily carburized manganese pig iron produced by a conventional iron removal method, such as a reducing melt in an electric furnace.

In the case when a removal of the iron from the ore considered for the supply of the electrolysis cell is not required, the process of reduction beforehand or of de-

carbonation may be carried out in the manner set forth below:

If the ore considered is pyrolusite based, the reduction to MnO will be already completed by keeping the ore, crushed to 28 mesh, for ½ hour at 950° C. in a reducing atmosphere containing 10% CO or other reducing gas; if the ore considered is decarbonated, it is not necessary for it to be crushed, because it will be automatically split by the heat. The reduction to MnO will be already completed by keeping said ore for ¼ hour at 800° C. in the presence of a nonoxidising atmosphere.

It must be well understood that the invention is not limited to the forms of embodiment described, and that many changes may be contemplated without departing from the scope of the present patent application.

Thus the cells described could possibly be used for the production of other metals than manganese, or the alloys thereof, and the electrolyte could contain minute additions of other oxides or salts than those comprised in the ternary systems cited hereinbefore such as BaO, B₂O₃, NaF, CaF₂ and having for their object to reduce the melting temperature thereof or to increase the electric conductivity thereof.

I claim:

1. A process for the production of manganese of low carbon content by electrolysis of a fused bath based on a system selected from the group consisting of the systems MnO-SiO₂-CaO, MnO-SiO₂-MgO, MnO-CaO-MgO, MnO-CaO-Al₂O₃ and MnO-MgO-Al₂O₃ and complex systems based on said systems.

2. A process according to claim 1, in which the fused bath is formed by the system MnO-SiO₂-CaO and the ratio by weight of lime with reference to the silica is at least .75:1.

3. A process according to claim 1, in which the fused bath is formed by the system CaO-MgO-SiO₂-Al₂O₃ and the weight ratio of lime and magnesia with reference to the silica and alumina is at least .75:1.

4. A process according to claim 1, in which the temperature of the bath is less than 1500° C. and the criteria of the electrolysis is adjusted so as to achieve a nonanodic effect condition in said bath.

5. A process according to claim 1, in which electrolyte bath is subjected to a preliminary electrolysis in order to remove therefrom metals which are more easily reducible than manganese as an alloy with manganese and then subjecting the electrolyte purified in this manner to a second electrolysis to produce manganese of higher purity.

6. A process according to claim 1, in which at least one metal having an affinity for oxygen about that of manganese is introduced in the electrolytic bath whereby said metal or metals are deposited at the cathode simultaneously with the manganese, as an alloy thereof.

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U.S. Cl. X.R.

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