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(54) **SEMI-CONTINUOUS RARE EARTH METAL PRODUCTION**

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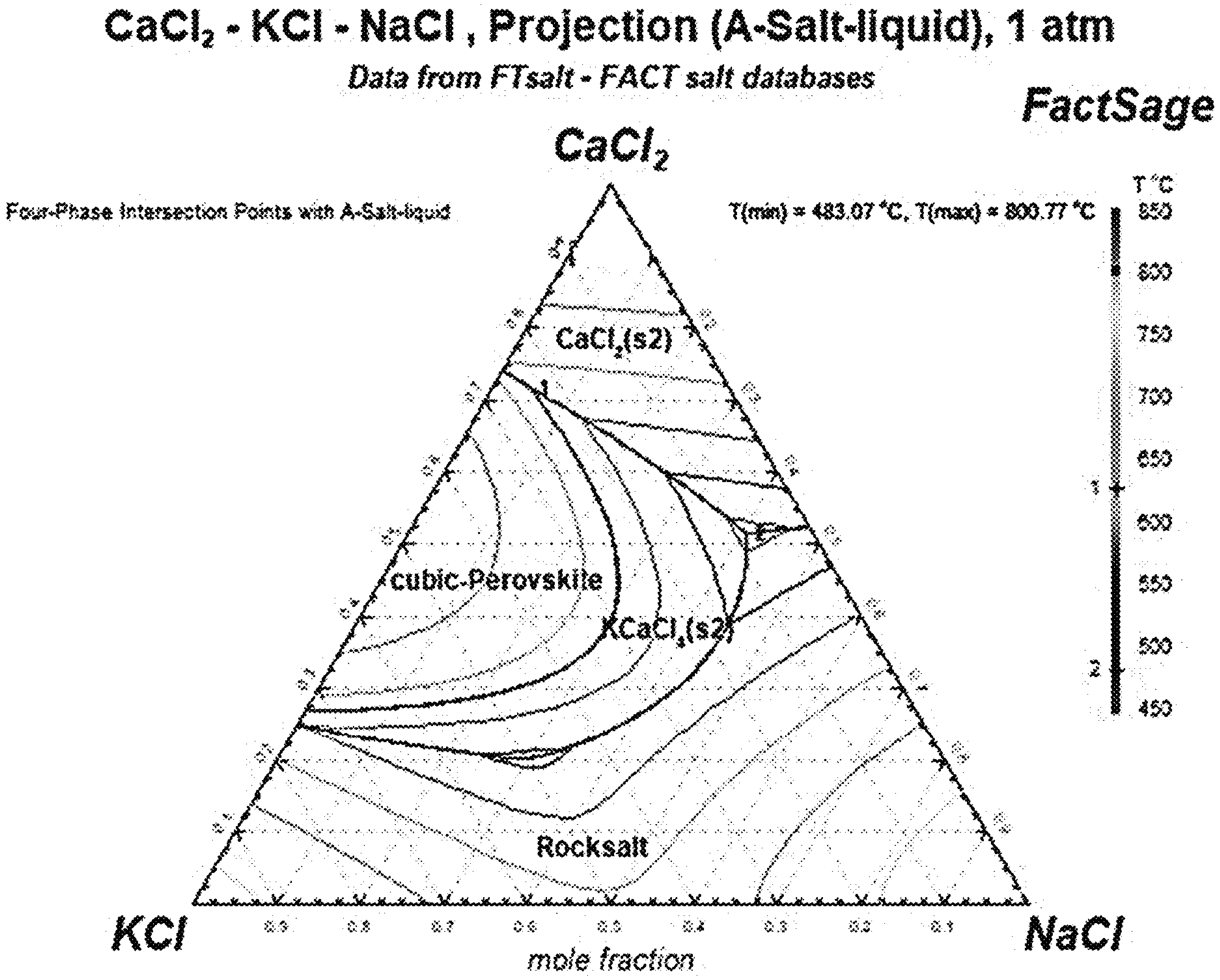
(57) **ABSTRACT**

The present disclosure relates to a low temperature, semi-continuous process for producing high purity rare earth metals and alloys in molten salts. Rare earth metals and alloys are reduced from the corresponding rare earth halide in molten salts in a semi-continuous process. An air stable pellet or ingot can be fed into molten salts and reduced through metallothermic reduction or electrolysis. The formation of an air stable feedstock minimizes handling concerns of the hygroscopic rare earth salts, allowing the reduction process to be run in a semi-continuous process. The process can optionally include the addition of alloying elements such as magnesium, iron and zinc reduce the required processing temperature.



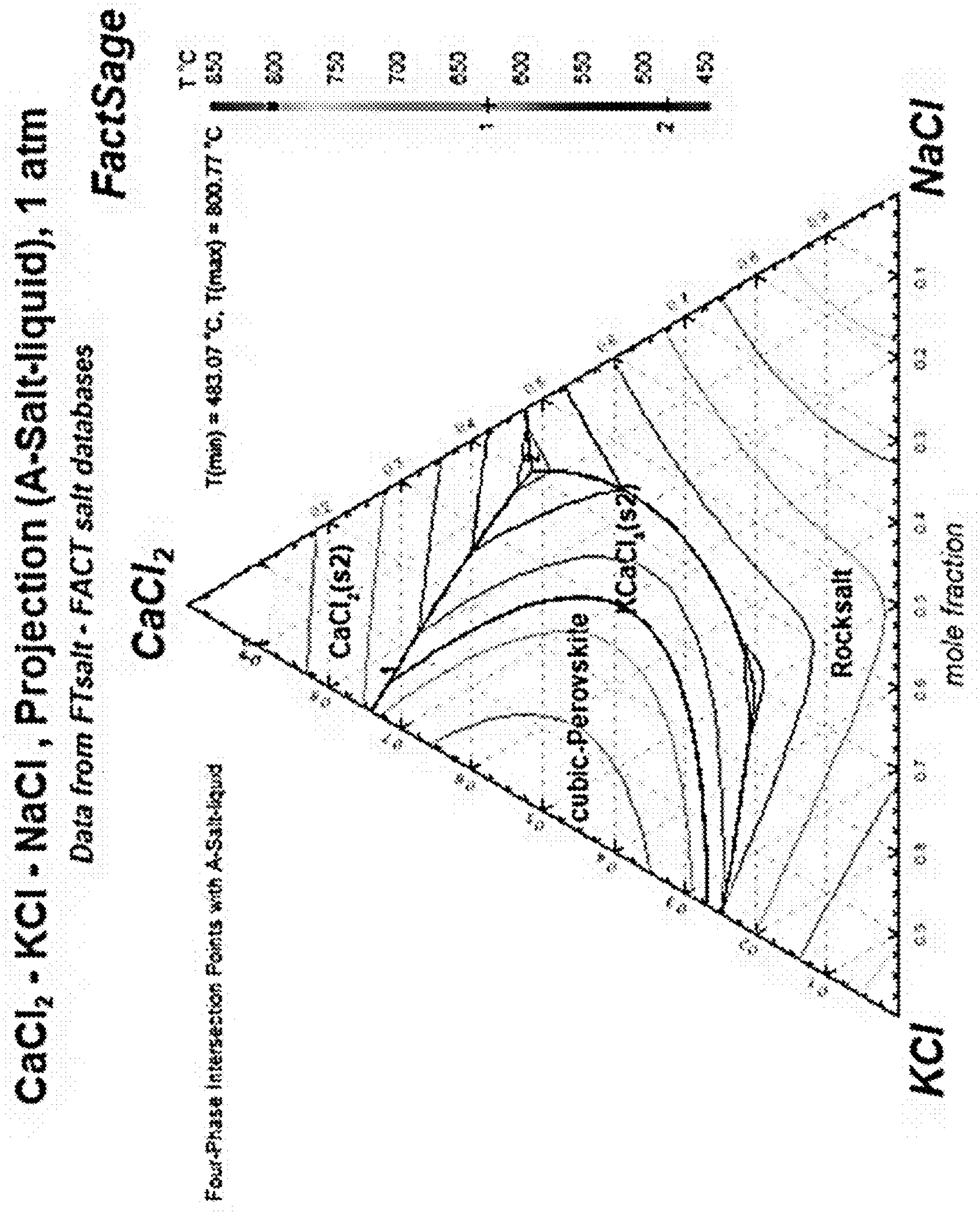

CaCl$_2$ - KCl - NaCl , Projection (A-Salt-liquid), 1 atm
Data from FTsalt - FACT salt databases
FactSage
Four-Phase Intersection Points with A-Salt-liquid
T(min) = 483.07 °C, T(max) = 800.77 °C
T °C
850
800
750
700
650
600
550
500
450
1
2
CaCl$_2$
KCl
NaCl
CaCl$_2$(s2)
KCaCl$_3$(s2)
cubic-Perovskite
Rocksalt
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
mole fraction

FIG. 1

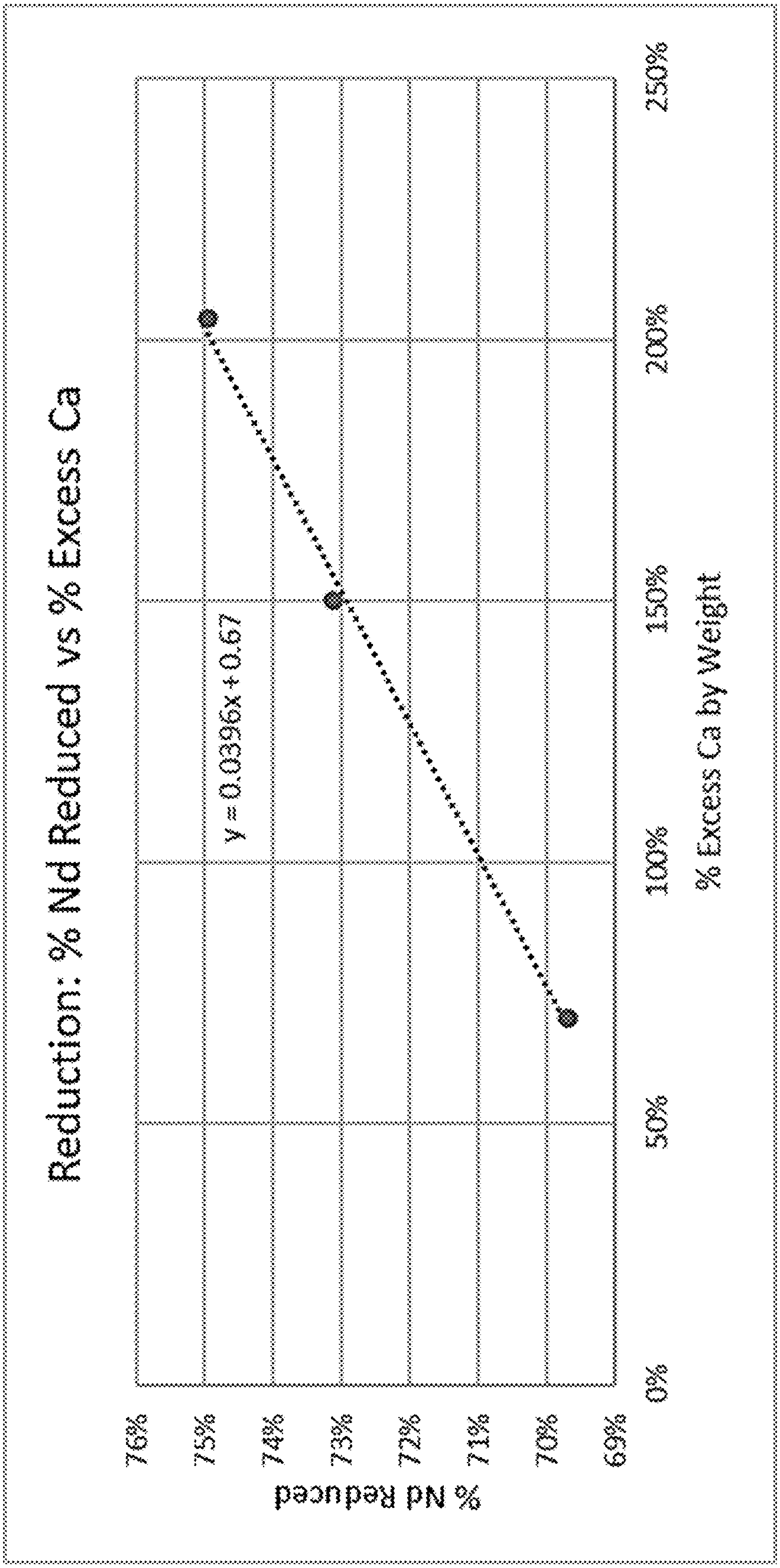

Reduction: % Nd Reduced vs % Excess Ca
y = 0.0396x + 0.67
% Nd Reduced
76%
75%
74%
73%
72%
71%
70%
69%
0%
50%
100%
150%
200%
250%
% Excess Ca by Weight

FIG. 2

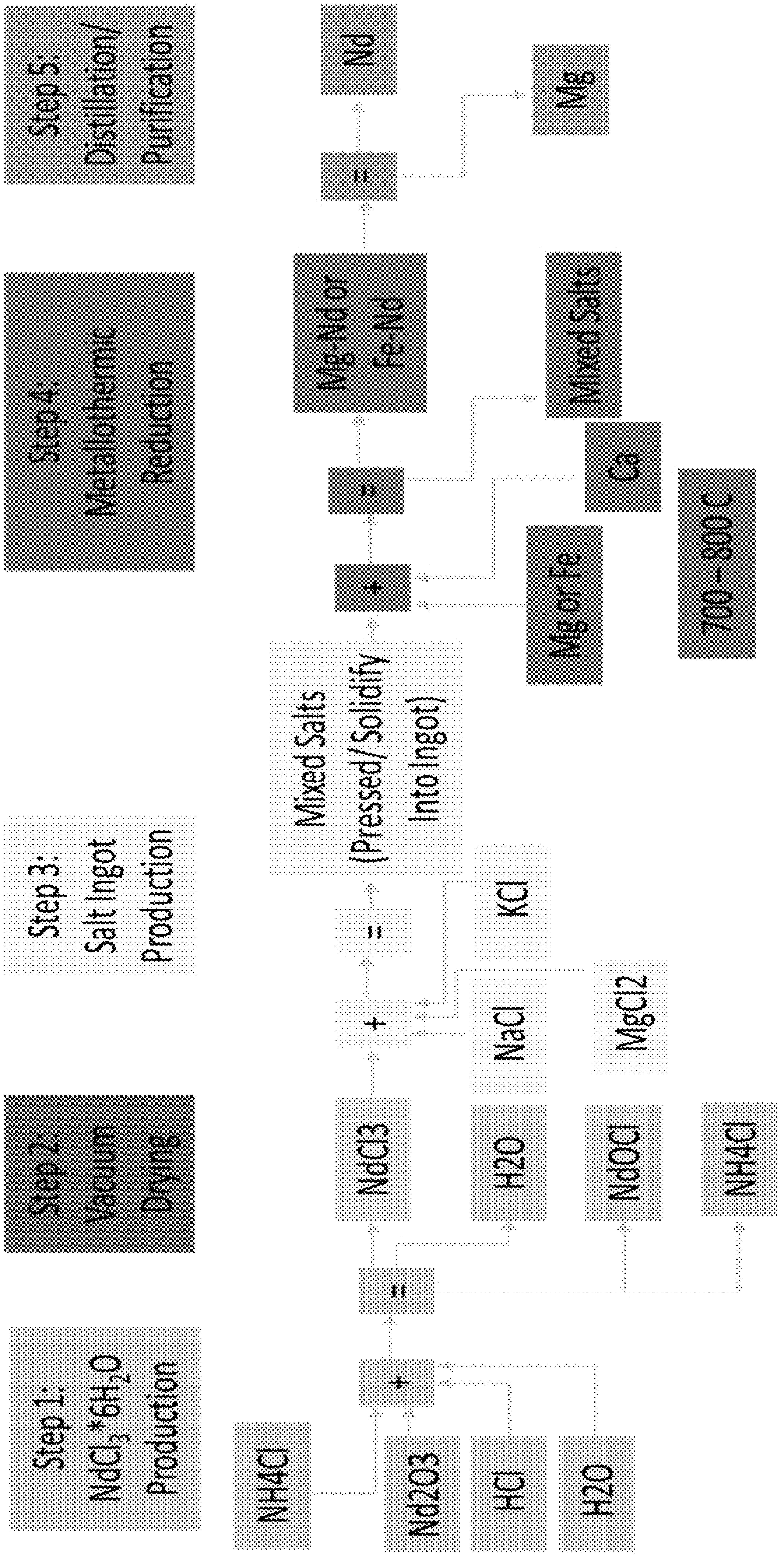

Step 1: $NdCl_3*6H_2O$ Production
NH4Cl
Nd2O3
HCl
H2O
+
=
Step 2: Vacuum Drying
NdCl3
H2O
NdOCl
NH4Cl
+
NaCl
KCl
MgCl2
=
Step 3: Salt Ingot Production
Mixed Salts (Pressed/Solidify Into Ingot)
Step 4: Metallothermic Reduction
+
Mg or Fe
Ca
700 – 800 C
=
Mixed Salts
Mg-Nd or Fe-Nd
Step 5: Distillation/ Purification
=
Nd
Mg

FIG. 3

SEMI-CONTINUOUS RARE EARTH METAL PRODUCTION

[0001] The present disclosure claims priority on U.S. Provisional Patent Application Ser. No. 63/359,058 filed Jul. 7, 2022, which in incorporated herein by reference.

[0002] This invention was made with U.S. government support under Subcontract SC-21-543. The U.S. government has certain rights in the invention.

[0003] The present disclosure relates to a low temperature, semi-continuous process for producing high purity rare earth metals and alloys in molten salts. For example, anhydrous neodymium chloride can be mixed with a mixture of metal salts (e.g., eutectic metal salts, etc.) to produce an air stable pellet or ingot. This air stable pellet or ingot can then be fed into molten salts and reduced through a metallothermic reduction or by electrolysis. The formation of an air stable feedstock can be used to minimize handling concerns of the hygroscopic rare earth salts, thereby allowing the reduction process to be run in a semi-continuous process. The process can optionally include the addition of alloying elements such as, but not limited to, magnesium, iron, and/or zinc to optionally reduce the processing temperature to less than 800° C.

BACKGROUND

[0004] Rare earth metals (RE) commonly are processed by conversion of the oxide into a halide salt, typically a fluoride salt, and then reduced in molten salts using an electrolytic process. While electrolysis is commonly used for producing rare earth metals, there are several key disadvantages. The electrodes that are required to process the rare earth metals are expensive. Also, during the processing of the rare earth metals, the electrodes are consumed, thus requiring frequent replacement. Electrolytic reduction during the processing of rare earth metals also requires temperatures that are generally greater than 1000° C. and, thus, limit the materials that can be safely used in production of the rare earth metals. Furthermore, the required use of high temperatures during the processing of rare earth metals increases the energy consumption and cost to process the rare earth metals.

[0005] Other process challenges required during the processing of rare earth metals include 1) the handling of dangerous fluoride compounds, 2) low yield limits of less than 50% for rare earth recovery, and 3) high electrical power costs due to the low current efficiencies that drive the reduction reaction.

[0006] Another process used to recover rare earth metals is a metallothermic reduction process. Such processes typically use calcium to reduce rare earth halides or oxides in a molten salt. However, these processes can only be run in batch processes (compared to the electrolytic reduction process which can be run continuously if the metal and salts can be balanced during reaction). However, one major advantage for using the metallothermic reduction process compared to the electrolytic reduction process is the high process yield. Typically, a yield of greater than 90% can be achieved using the metallothermic reduction process for the recovery of rare earth metals.

[0007] After the recovery of the rare earth metals, the rare earth metals are separated from one another to form the desired high purity rare earth oxides. Thereafter, the separated rare earth oxides are reduced from their compound state to the respective rare earth metals. Generally, the reduced rare earth metals have a purity of at least 95 atomic percent or purer depending on the contaminants. Such purity levels are generally required for the rare earth metals to be useful in permanent magnets and other applications.

[0008] In the past, the reduction process was a complicated and expensive process, thereby adding substantial cost to the production of pure rare earth metals. One type of reduction of rare earth halides was accomplished by the reaction with more electropositive metals such as calcium, sodium, lithium, and potassium. However, rare earth metals have a great affinity for elements such as oxygen, sulfur, nitrogen, carbon, silicon, boron, phosphorous, and hydrogen. As such, the reduced rare earth metals produced from rare earth halides were highly contaminated with very stable compounds of the rare earths and oxygen, sulfur, nitrogen, carbon, silicon, boron, phosphorous, and/or hydrogen. The yields from the reduction of rare earth halides were also very low (about 25 percent). Also, the reduced metal existed as small nuggets surrounded by alkali chloride slag which further increased the time, complexity, and cost to recover the pure rare earth metal.

[0009] Currently, both electrolytic and metallothermic (non-electrolytic) processes are employed to commercially reduce rare earth halides (chlorides or fluorides) to rare earth metals pure enough for use in industry. Due to the highly hygroscopic nature of the chlorides, commercial processes tend to adopt the use of fluoride and include the electrolytic reduction of the fluoride in alkali metal salts, or the metallothermic reduction of rare earth fluoride in metal salts.

[0010] The disadvantages of using the electrolytic process to recover pure rare earth metal include 1) the use of expensive electrodes which are eventually consumed, 2) high temperature cell operation (generally greater than 1000° C.), 3) low current efficiencies resulting in high power costs, and 4) low yield of rare earth metal from the rare earth salt (generally 40 percent or less of the rare earth metal in the salt can be recovered). The rare earth-fluoride reduction process also requires careful control of a temperature gradient in the electrolytic salt cell to cause solidification of the rare earth metal nodules. An advantage of electrolytic processes is that it can be made to run by tapping the reduced metal and refortifying the salt bath. Consequently, the electrolytic process does not show much promise for reducing the cost of rare earth metal recovery or increasing the availability of magnet-grade rare earth metals.

[0011] The most common metallothermic reduction processes for the recovery of rare earth metal are 1) the reduction of rare earth-fluorides with calcium metal (i.e., a calciothermic process), or 2) the reduction-diffusion of rare earth-oxide with calcium hydride or calcium metal (i.e., emerging Cambridge FCC process). Disadvantages of these two metallothermic reduction processes are 1) both metallothermic reduction processes are batch processes, 2) both must be conducted in a non-oxidizing atmosphere, and 3) both are energy intensive. When using a reduction-diffusion process, the recovered rare earth product is a powder which must be washed repeatedly to purify the powder before it can be used. As such, both metallothermic reduction processes involve many steps, thus increasing time and cost of processing. One advantage of metallothermic reduction processes is that the yield of rare earth metal from the fluoride is generally greater than 90 percent. However, fluorides are highly corrosive and toxic, particularly byproducts of fluorides such as HF gas. Also, the cost of fluorine is higher compared to chlorine. Consequently, neither of these metallothermic reduction processes show much promise for reducing the cost of rare earth metal recovery or increasing the availability of magnet-grade rare earth metals.

SUMMARY OF THE DISCLOSURE

[0012] The present disclosure relates to a low temperature, semi-continuous process for producing high purity rare earth metals and alloys in molten salts. For example, anhydrous neodymium chloride can be mixed with a mixture of metal salts (e.g., eutectic metal salts, etc.) to produce an air stable pellet or ingot. This air stable pellet or ingot can then be fed into molten salts and reduced through a metallothermic reduction or by electrolysis. The formation of an air stable feedstock can be used to minimize handling concerns of the hygroscopic rare earth salts, thereby allowing the reduction process to be run in a semi-continuous process. The process can optionally include the addition of alloying elements such as, but not limited to, magnesium, iron, and/or zinc to optionally reduce the processing temperature to less than 800° C.

[0013] One non-limiting object of the present disclosure is directed to a process for producing rare earth metal (RE) or an alloy of rare earth metal (RE); said process is optionally a continuous or semi-continuous process; said process includes: a) adding to a reaction vessel an initial charge of a eutectic-forming metal that forms a eutectic with said RE; optionally adding calcium metal to said reaction vessel; said eutectic optionally has a metaling point of less than 1000° C.; b) adding to said reaction vessel an initial charge of anhydrous RE-chloride salt and/or RE-fluoride salt to form a charged mixture; optionally adding one or more alkali metal halides to said charged mixture; said charged mixture optionally has a melting point that is less than 1000° C.; c) heating said charged mixture in said reaction vessel; said temperature of said charged mixture in said reaction vessel is optionally greater than 700° C. and optionally less than 1000° C.; d) mixing said charged mixture in said reaction vessel to cause a reaction to convert the RE-chloride and/or RE-fluoride to RE metal and/or RE metal alloy and calcium chloride salt and/or calcium fluoride salt; e) removing a portion or all of the eutectic metal, rare earth metal, and/or rare earth alloy from said reaction vessel; optionally removing some or all of a salt mixture from said reaction vessel; and f) optionally adding additional eutectic-forming metal, alkali metal halides, calcium metal, RE-chloride salt and/or RE-fluoride salt to said reaction vessel, and then repeating the steps c-f to obtain additional amount of RE metal and/or RE metal alloy.

[0014] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE); said process is optionally a continuous or semi-continuous process; said process includes: a) providing a reaction vessel; b) providing a eutectic-forming metal; c) providing RE-chloride salt and/or RE-fluoride salt; d) providing a chloride and/or fluoride salt; e) adding said eutectic-forming metal, said RE-chloride salt and/or RE-fluoride salt, and said chloride and/or fluoride salt to said reaction vessel; f) causing said RE-chloride salt and/or RE-fluoride salt to react with other materials in said reaction vessel to form RE metal and/or RE metal alloy; and g) removing said RE metal and/or RE metal alloy from said reaction vessel.

[0015] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) that includes the step of adding calcium metal to the reaction vessel.

[0016] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said eutectic-forming metal is at least partially added as a master alloy that includes calcium.

[0017] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said eutectic-forming metal is melted in said reaction vessel prior to said addition of said calcium metal to said reaction vessel.

[0018] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said step of providing RE-chloride salt and/or RE-fluoride salt includes: i) providing Re oxide; ii) providing a chloride and/or fluoride salt; optionally providing a chloride acid and/or a fluoride acid; optionally providing water; iii) mixing together said RE oxide, chloride and/or fluoride salt, optional chloride acid and/or a fluoride acid, and optional water to cause said RE oxide to form said RE-chloride salt and/or RE-fluoride salt; said step of mixing optionally occurring in a vacuum to remove water byproduct and inhibit formation of RE-oxychloride and/or RE-oxyflouride; said step of mixing optionally subjected to heating to remove water byproduct and inhibit formation of RE-oxychloride and/or RE-oxyflouride; iv) optionally condensing of chloride and/or fluoride salt and said water in an optional cold trap to recovery of said chloride and/or fluoride salt; and, v) optionally vacuum drying said formed RE-chloride salt and/or RE-fluoride salt; said vacuum drying optionally occurs at a temperature of 100° C.-200° C.

[0019] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said eutectic-forming metal includes aluminum, iron, magnesium, zinc, and/or aluminum.

[0020] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said RE-chloride salt and/or RE-fluoride salt is in the form of a pellet or ingot and optionally includes alkali salts.

[0021] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said pellet or ingot has a melting point of no more than 1000° C.

[0022] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein i) said eutectic-forming metal, ii) said RE-chloride salt and/or RE-fluoride salt, iii) said chloride and/or fluoride salt, and iv) said optional calcium in said reaction vessel are heated to a temperature of no more than 1000° C.

[0023] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) that further includes the step of mixing and/or agitating i) said eutectic-forming metal, ii) said RE-chloride salt and/or RE-fluoride salt, iii) said chloride and/or fluoride salt, and iv) said optional calcium in said reaction vessel.

[0024] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) that further includes the step of adding alkali metal chlorides, alkali metal fluorides, calcium chloride, calcium fluoride, magnesium chloride, magnesium fluoride, metal halide chlorides, and/or metal halide fluorides to said reaction vessel.

[0025] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said RE-chloride salt and/or RE-fluoride salt is in the form of pellets or ingots.

[0026] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said pellets or ingots have a) a melting point of no more than 1000° C., b) a low surface area, and/or c) reduced moisture sensitivity.

[0027] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said alkali metal chlorides, alkali metal fluorides, calcium chloride, calcium fluoride, magnesium chloride, magnesium fluoride, metal halide chlorides, and/or metal halide fluorides are included in said pellets or ingots.

[0028] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said RE metal and/or RE metal alloy is allowed to separate from other materials in said reaction vessel prior to removal of said RE metal and/or RE metal alloy from said reaction vessel.

[0029] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein a time for allowing said separation of said RE metal and/or RE metal alloy from other materials in said reaction vessel is at least 10 minutes, and optionally 10-60 minutes.

[0030] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said RE metal and/or RE metal alloy and any salt compounds in said reaction vessel are removed separately from said reaction vessel.

[0031] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said RE metal and/or RE metal alloy and any salt compounds in said reaction vessel are removed simultaneously, without separation, from said reaction vessel.

[0032] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) that further includes the step of i) purifying said RE metal and/or RE metal alloy and/or ii) separating said RE metal and/or RE metal alloy form said salt compounds; said step of purifying and/or separating optionally includes the use of a) centrifugal force, b) gas bubbling and/or c) distillation.

[0033] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) that further includes the step of adding sodium to said reaction vessel to at least partially regenerate calcium metal; said regeneration of said calcium metal optionally obtained in situ by a reduction of CaCl2.

[0034] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein chloride salt and/or fluoride salt is at least partially removed from said reaction vessel is at least partially purified by partial crystallization of $CaCl_2$) to optionally within 10 degrees (e.g., 0-10° C. and all values and ranges therebetween) of the $KCl—NaCl—CaCl_2$) eutectic.

[0035] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) that further includes the step of removing aluminum, iron, magnesium, zinc, and/or aluminum from said RE metal alloy; said step of removing aluminum, iron, magnesium, zinc, and/or aluminum from said RE metal alloy is optionally conducted with use of a multi-stage system; said multi-stage system optionally includes successively higher vacuum levels that draw on each successive evaporative chamber, and/or limited additional heat is added to each successive evaporative chamber to allow for recapture and reuse of latent heat during said removal process.

[0036] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein a condenser of one of said chambers acts to provide a majority of heat for a successive evaporative chamber.

[0037] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said multi-stage system includes 3-6 evaporative chamber.

[0038] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein no calcium metal is added to said reaction vessel; and any calcium in said reaction vessel is optionally formed by sodium additions to said reaction vessel which causes calcium-containing salts to react with said sodium and form calcium metal in said reaction vessel.

[0039] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein some or all of said RE-chloride salt is replaced with RE-oxychloride salt and/or RE-oxyfluoride salt.

[0040] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said reaction vessel is at least partially formed of iron.

[0041] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said reaction of said RE-chloride salt and/or RE-fluoride salt in said reaction vessel occurs at a temperature of no more than 1000° C., and optionally no more than 850° C.

[0042] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein said reaction vessel is partially or fully coated with a ceramic coating; said ceramic coating optionally including one or more materials selected from the group of yttrium oxide, zirconium oxide, calcium oxide, and magnesium oxide.

[0043] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) wherein a time of reaction of said RE-chloride salt and/or RE-fluoride salt in said reaction vessel is at least 5 minutes, and optionally about 5-30 minutes.

[0044] In another and/or alternative non-limiting object of the present disclosure is directed to a method for producing rare earth metal (RE) or an alloy of rare earth metal (RE) Other aspects, advantages, and novel features of the present disclosure will become apparent from the following detailed description and figures of the disclosure.

BRIEF DESCRIPTION OF DRAWINGS

[0045] Reference may now be made to the drawings which may illustrates a non-limiting embodiments that the disclosure may take in physical form and in certain parts and arrangement of parts wherein:

[0046] FIG. **1** illustrates a KaCl—NaCl—$CaCl_2$) phase diagram.

[0047] FIG. **2** is a graft that illustrates the relationship of the amount of Nd that is reduced in relationship to the amount of excess Ca added to the mixture in the metallothermic reaction.

[0048] FIG. **3** illustrates one non-limiting process to produce rare earth metal Nd in accordance with the present disclosure.

DETAILED DESCRIPTION OF NON-LIMITING EMBODIMENTS OF THE DISCLOSURE

[0049] A more complete understanding of the articles/devices, processes and components disclosed herein can be obtained by reference to the accompanying drawings. These figures are merely schematic representations based on convenience and the ease of demonstrating the present disclosure, and are, therefore, not intended to indicate relative size and dimensions of the devices or components thereof and/or to define or limit the scope of the exemplary embodiments.

[0050] Although specific terms are used in the following description for the sake of clarity, these terms are intended to refer only to the particular structure of the embodiments selected for illustration in the drawings and are not intended to define or limit the scope of the disclosure. In the drawings and the following description below, it is to be understood that like numeric designations refer to components of like function.

[0051] The singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise.

[0052] As used in the specification and in the claims, the term “comprising” may include the embodiments “consisting of” and “consisting essentially of.” The terms “comprise(s),” “include(s),” “having,” “has,” “can,” “contain(s),” and variants thereof, as used herein, are intended to be open-ended transitional phrases, terms, or words that require the presence of the named ingredients/steps and permit the presence of other ingredients/steps. However, such description should be construed as also describing compositions or processes as “consisting of” and “consisting essentially of” the enumerated ingredients/steps, which allows the presence of only the named ingredients/steps, along with any unavoidable impurities that might result therefrom, and excludes other ingredients/steps.

[0053] Numerical values in the specification and claims of this application should be understood to include numerical values which are the same when reduced to the same number of significant figures and numerical values which differ from the stated value by less than the experimental error of conventional measurement technique of the type described in the present application to determine the value.

[0054] All ranges disclosed herein are inclusive of the recited endpoint and independently combinable (for example, the range of “from 2 grams to 10 grams” is inclusive of the endpoints, 2 grams and 10 grams, all the intermediate values and all intermediate ranges).

[0055] The terms “about” and “approximately” can be used to include any numerical value that can vary without changing the basic function of that value. When used with a range, “about” and “approximately” also disclose the range defined by the absolute values of the two endpoints, e.g., “about 2 to about 4” also discloses the range “from 2 to 4.” Generally, the terms “about” and “approximately” may refer to plus or minus 10% of the indicated number.

[0056] Percentages of elements should be assumed to be percent by weight of the stated element, unless expressly stated otherwise.

[0057] In accordance with one non-limiting aspect of the present disclosure, the present disclosure relates to a low temperature (e.g., less than 1000° C.; 600-995° C. and all values and ranges therebetween), semi-continuous process for producing high purity rare earth metals and alloys in molten salts. For example, anhydrous neodymium chloride can be mixed with a mixture of metal salts (e.g., eutectic salts, etc.) to produce an air stable pellet or ingot. As can be appreciated, other or additional types of rare earth chlorides can be mixed with eutectic salts to produce an air stable pellet or ingot. This air stable pellet or ingot can then be fed into molten salts and reduced through a metallothermic reduction or by electrolysis. The formation of an air stable feedstock can be used to minimize handling concerns of the hygroscopic rare earth salts, thereby allowing the reduction process to be run in a semi-continuous process. The process can optionally include the addition of alloying elements such as, but not limited to, magnesium, iron, and/or zinc to reduce the required processing temperature to less than 1000° C. (e.g., less than 800° C.).

[0058] In accordance with another and/or alternative non-limiting aspect of the present disclosure, the present disclosure resolves several issues with prior art processes for the recovery of rare earth metals. The present disclosure is related to a continuous or semi-continuous process for a chloride metallothermic reduction process that significantly addresses the issues associated with chloride water absorption, and the cost of prior art batch processes. As can be appreciated, the process for the recovery of rare earth metals can optionally be conducted as a batch process. The process in accordance with the present disclosure can also optionally be adapted for use with an electrolytic process. The present disclosure relates to process that uses low melting salt mixtures of rare earth chloride and NaCl and/or KCl (and optionally also or alternatively with $CaCl_2$), $MgCl_2$ and/or other metal halides). As will be appreciated, the present disclosure will be described with particular reference to a chloride metallothermic reduction process; however, it will be appreciated that the present disclosure also is equally applicable to a fluoride metallothermic reduction process wherein fluoride salts are used instead of chloride salts. The chloride metallothermic reduction process is generally more desirable to the fluoride metallothermic reduction process in that the fluoride salts are generally more expensive than the chloride salts, and the chloride byproducts (e.g., HCl, etc.) formed from the chloride metallothermic reduction process are less harsh than the fluoride byproducts (e.g., HF, etc.) formed from the fluoride metallothermic reduction process.

[0059] In accordance with another and/or alternative non-limiting aspect of the present disclosure, the improved chloride metallothermic reduction process includes the use of a calciothermal reduction from rare earth chlorides in molten salts and using one or more additional metals to reduce the processing temperatures.

[0060] In accordance with another and/or alternative non-limiting aspect of the present disclosure, high purity or commercial purity metals oxides of rare earth lanthanides, IIIB, IVB, or 5B elements that include, but are not limited to, lanthanum, cerium, praseodymium, neodymium, dysprosium, europium, promethium, lutetium, gadolinium, terbium, erbium, holmium, ytterbium, scandium, yttrium, can be used in the improved chloride metallothermic reduction process. These metal oxides can be reacted to form metal chlorides that are or include rare earth chlorides, which can be mixed and reacted with molten halide salts. Calcium or sodium can optionally be used as the reductant in the molten chloride salts. As stated above, these metal oxides can alternatively be reacted to form metal fluorides that are or include rare earth fluorides, which can be mixed and reacted with molten halide salts, and calcium or sodium can optionally be used as the reductant in the molten fluoride salts.

[0061] In accordance with another and/or alternative non-limiting aspect of the present disclosure, the temperature of the improved chloride metallothermic reduction process can be reduced by the further additions of eutectic-forming metals such as Fe, Mg, Zn and/or Al metal to the mixture of rare earth chlorides, metal oxides, and molten chloride salts. The addition of the eutectic-forming metals to the mixture results in the chloride metallothermic reduction process to occur at temperatures of no more than 1000° C. (e.g., 600° C.-1000° C. and all values and ranges therebetween), and typically no more than 850° C. This processing temperature reduction is the result of the eutectic-forming metals forming a low melting liquid that contains the reduced rare earth metal. Because of the reduced processing temperatures, steel crucibles can optionally be used in the process, thereby lowering the processing costs. In prior art processes wherein the processing temperatures exceeded 1000° C., steel crucibles could not be used and special high-cost metal alloy crucibles were required. Because the calico thermal reduction is an exothermic reaction, the only significant heat input during the processing of the rare earth metals is the heat required to melt the initial salt charge. As such, heating costs are further reduced by use of the formation of a low melting liquid containing the reduced rare earth metal.

[0062] In accordance with another and/or alternative non-limiting aspect of the present disclosure, the rare earth chlorides can be produced by digestion of the rare earth oxide in HCl, followed by vacuum drying under staged temperature with or without the addition of NH_4Cl. Alternatively, the rare earth chlorides can be prepared via the direct reaction of the rare earth oxide with NH_4Cl. In some cases, reaction with chlorine in the presence of carbon is preferable for formation of the rare earth chloride. For handling, the rare earth chloride can optionally be melted into a eutectic with a chlorine salt such as, but not limited to, a NaCl—KCl mixture, thus allowing the rare earth chloride to be cast into ingots at relatively low temperatures for furnace charging.

[0063] In accordance with another and/or alternative non-limiting aspect of the present disclosure, several rare earth metals have high melting points (e.g., above 1000° C.), and the processing temperature of such rare earth metals can be reduced by use of eutectic metal additions. For example, unalloyed Nd metal has a melting temperature of about 1025° C. The chloride metallothermic reduction process can optionally be operated at such high temperatures to obtain pure rare earth metal at high yields. However, by adding eutectic metal additions such as iron, zinc, magnesium, aluminum, or other non-rare earth metals to the reduction vessel, an alloy having a lower melting-point (e.g., less than 1000° C.) than the pure rare earth metal is formed with the recovered rare earth metal. For example, iron (Fe) forms a low-melting eutectic alloy with neodymium (11.5 weight percent Fe, balance Nd; m.p. about 640° C.). Likewise, zinc (Zn) also forms a low-melting eutectic alloy with neodymium (11.9 weight percent Zn, balance Nd; m.p. about 630° C.). A near-eutectic collection pool of iron and rare earth alloy is very efficient for aggregation-reduced rare earth elements. A Nd—Fe eutectic alloy may optionally be directly alloyed with additional iron and boron to make magnets having the optimum Nd_2FeB magnetic phase. Metals can be optionally added to the reaction vessel as needed to maintain a desired composition in the collection pool. If it is desired to lower the melting point of the recovered rare earth metal, but not retain the metal added to do so, a metal with a boiling point much lower than the boiling point of the recovered rare earth can be added to the reaction vessel. For example, Zn boils at 907° C., magnesium boils at 1090° C., and Nd boils at 3150° C. A low-melting metal such as zinc or magnesium can be readily separated from the recovered rare earth metal by simple distillation.

[0064] In accordance with another and/or alternative non-limiting aspect of the present disclosure, the reaction vessel used to recover the rare earth metal can be made from traditional metals such as molybdenum, tantalum, and/or zirconium. However, due to the lower processing temperature for the recovery of the rare earth metals in accordance with the present disclosure, the reaction vessel can optionally be made of a lower cost iron or steel. In one non-limiting embodiment, when the mixture includes zinc and/or magnesium additions, an iron reaction vessel can be used; however, this is not required. In another non-limiting embodiment, when the mixture has a melting temperature of less than 1000° C., an iron reaction vessel can be used; however, this is not required.

[0065] In accordance with another and/or alternative non-limiting aspect of the present disclosure, the reaction vessel used to recover the rare earth metal can optionally be made from iron such that the recovered rare earth metal partially or fully alloys with a portion of the iron of the reaction vessel. Such iron alloyed rare earth metals can be used for the formation of magnets; however, such a process will result in the slow consumption of the reaction vessel over time.

[0066] In accordance with another and/or alternative non-limiting aspect of the present disclosure, the reaction vessel used to recover the rare earth metal can be made from iron or other metal and a portion or all of the reaction vessel can optionally be coated with a ceramic material or refractory metal to reduce the rate of consumption of the metal used to form the reaction vessel (e.g., iron, etc.) during the recovery of the rare earth metal. Generally, the coating has a melting or degradation temperature that is greater than the melting point of iron. Non-limiting coatings include, but are not limited to, yttria, molybdenum, rhenium, tantalum, tungsten, and/or stabilized or partially stabilized zirconia.

[0067] In accordance with another and/or alternative non-limiting aspect of the present disclosure, there is provided a novel method of using Group I and II reducing metals (e.g., sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, and/or barium) to reduce rare earth chlorides. The reducing metal (M) can be added directly to the reaction vessel to effect reduction of the rare earth chloride by the following reaction:

$$x\mathrm{RECl}n+y\mathrm{M}\rightarrow x\mathrm{RE}+y\mathrm{MCl}$$

[0068] where $n \cdot x = y$

[0069] The $CaCl_2$) content of the bath is generally maintained above 70 vol. %. Na or K may be added to produce Ca metal in the reaction vessel by the reaction $CaCl_2$)+2M→2MCl+Ca, wherein M is Na and/or K. Where any substantial amount of oxychloride is present, calcium is generally present either by direct addition or by an exchange reaction with sodium since the oxychloride is not directly reduced by Group I metals.

[0070] In accordance with another and/or alternative non-limiting aspect of the present disclosure, the one or more reducing metals are optionally stirred and/or agitated with the rare earth chloride and the salt bath in the reaction vessel to keep all constituents in physical contact with one another. Agitation such as rapid stirring causes the metal from the collection pool to mix with the salt bath. The metal from the pool can agglomerate with the rare earth metal that is created by the reduction reaction. When agitation is stopped, the relatively dense rare earth metals become part of the collection pool and settles below the salt bath and any unreacted reducing metal in the reaction vessel. At the bottom of the reaction vessel, the rare earth metals can optionally be tapped while molten for removal from the reaction vessel and/or removed from the reaction vessel after solidification.

[0071] In accordance with another and/or alternative non-limiting aspect of the present disclosure, one or more eutectic metal additions can also be added to the mixture. In one non-limiting embodiment, the temperature range of the mixture in the reaction vessel is generally from 650-850° C. At such temperatures, the loss of the reducing metal during the processing is not a serious problem. Also, at such temperatures, the wear on the reaction vessel is reduced. Such temperature range is suitable for reducing, for example, $NdCl_3$ to Nd metal when eutectic metal additions are used since Nd—Fe, Nd—Mg, and Nd—Zn eutectic temperatures are below 700° C. Similarly, the melting temperatures of rare earth chlorides and rare earth oxychlorides are reduced when these compounds are dispersed in chloride salts of sodium, calcium, and/or potassium. Higher processing temperatures can be used; however, there are several advantages for processing the rare earth metal at lower temperatures. For good separation of reduced metal from the flux, the reaction temperature should be a) above the melting point of the reduced metal, b) above the melting point of the reduced metal alloy, or c) co-reduced with another metal.

[0072] In accordance with another and/or alternative non-limiting aspect of the present disclosure, one processing sequence in accordance with the present disclosure can include a) charging the reaction vessel with an initial mixture of rare earth chloride salt, b) melting and heating the mixture in the reaction vessel to 700-900° C., and generally 750-850° C., c) adding calcium plus eutectic amounts or slight excess of Fe, Mg, Zn, and/or Al to the reaction vessel, d) agitating the salt-metal mixture to intimately contact the rare earth chloride and Ca, e) terminating agitation so that the metal and salt mixtures can be segregated into layers, f) pumping, tapping, or pouring each layer out of the reaction vessel so that the rare earth metal and/or rare earth metal alloy can be removed from the reaction vessel, and g) optionally adding additional rare earth chloride salt and metals to the reaction vessel to further process the rare earth metal. Alternatively, Na or K can be added to the rare earth salt to generate Ca metal, to partially or fully substitute the separate addition of Ca metal to the reaction vessel.

[0073] In accordance with another and/or alternative non-limiting aspect of the present disclosure, the $CaCl_2$) byproduct formed in the reaction vessel can optionally be separated from the mixed salt stream using controlled solidification/precipitation to remove the majority of the $CaCl_2$). As illustrated by the phase diagram of FIG. **1**, $CaCl_2$) can be removed to the eutectic 2, at approximately 475° C. and 40:40:20 KCl:NaCl:$CaCl_2$) molar ratios.

[0074] In accordance with another and/or alternative non-limiting aspect of the present disclosure, the salt mixture that is fed to the reactor vessel can optionally include a mixture of 50:50 NaCl:KCl (+/−5%) and the rare earth chloride. A 20 wt. % $CaCl_2$) eutectic can optionally also be used. To purify the rare earth salt, the molten salt in the reaction vessel is solidified to a temperature corresponding to roughly 20 wt. % $CaCl_2$). This 40:40:20 mixture by weight is then used to prepare additional feedstock by adding rare earth chloride to allow for semi-continuous processing and full recycle of the salt generated. Measurement of oxygen content in the reaction vessel can optionally be used as a quality control step, as less reactive oxychloride can be formed during handling and processing; as it builds up in the reaction vessel, the mixture in the reaction vessel must be purified or replaced.

[0075] In accordance with another and/or alternative non-limiting aspect of the present disclosure, the reduction process can optionally be run in semi-continuous mode, adding a Ca+metal and metal eutectic additions in a near continuous fashion until reaching at least 100% (e.g., 100%-140% and all values and ranges therebetween; 120%) (based on stoichiometric calcium) of the rare earth chloride charge. Alternatively, the entire maximum furnace charge can be added, followed by reaction, and then periodic removal of products and addition of new charge of metal and salt. Reaction occurs during intense mixing or agitation. After a reaction/mixing time based on optimizing yields, agitation and mixing conditions are changed to allow the metal and salt layers to separate. In one non-limiting example, adding $NdCl_3$ stoichiometric or rare earth chloride rich-eutectic salt to the reaction vessel while the reaction vessel is still charged can be used to continue the process until the salt must be lowered/removed. In another non-limiting example, the metal can be charged in the reaction vessel, thereby keeping the metal hot and using the heel metal to enhance heat transfer and faster melting of additional charges. Generally, it can take 3-5 hours to melt an initial furnace charge, and then productivity is 300-600 lbs./hr. (Mg).

[0076] In accordance with another and/or alternative non-limiting aspect of the present disclosure, in order to keep temperatures below 850° C. in the reaction vessel, pre-alloying of the calcium with Zn or Mg or Na (e.g., 5-20 wt. % Na and all values and ranges therebetween) can be used to reduce the melting temperature of the metal additions to the reaction vessel below 850° C. (e.g., below 800° C.). Such reduced operating temperatures can result in the increased life of the reaction vessel, such as an iron reaction vessel. Prealloying with the Ca with Na allows for the generation of free Ca in the melt in the reaction vessel, thereby allowing larger yields of the recovered rare earth metal for a given crucible capacity. Similarly, shifting from Ca addition to increasing Na content additions (up to and including pure Na) reduces salt/dross removal. Sodium can also be less expensive than calcium, even though more is required (2×), and can optionally be fed directly as a liquid feed for ease of addition. When Fe, Mg, and/or Zn are added to the reaction vessel, master alloys of RE-Fe, RE-Mg, and/or or RE-Zn are formed. These master alloys may also be contaminated with Ca. When Zn or Mg are added to the reaction vessel, the master alloy can be purified using vacuum distillation, which removes the majority of the Mg or Zn (e.g., 80-99+% removal of Mg and/or Zn and all values and ranges therebetween) from the master alloy, as well as removal of a majority of the calcium and any sodium in the master alloy (e.g., 80-99+% removal of Ca and/or Na and all values and ranges therebetween). The Mg and Mg—Ca that are removed by the vacuum distillation process can optionally be recycled for use in further processing, or used in producing magnesium or aluminum alloys, steel reduction, or other applications. Any iron in the master alloy can be purified from Ca and residual chlorides by zone refining or vacuum arc melting (e.g., 80-99+% removal of Fe and all values and ranges therebetween). Pure rare earth metal (e.g., 95+% pure) can be produced from RE-Mg or RE-Zn master alloys by vacuum distillation of the Mg or Zn, followed by zone refining or vacuum melting to remove residual Mg, Ca, and chlorides. As can be appreciated, other or additional processes can be used to remove metals and impurities from the master alloys to form pure (e.g., 95+% pure) rare earth metal from the master alloy.

Example A

[0077] In one non-limiting example, there is provided a method for metallothermic reduction that includes the use of a gas-fired furnace, a stainless steel crucible, and specific additives to enhance the reduction process. The reduction is performed under controlled conditions to improve the yield of a magnesium alloy containing neodymium (Nd) and calcium (Ca).

[0078] In the experimental setup, vacuum dried $NdCl_3$ is subjected to metallothermic reduction in the gas-fired furnace. The furnace contains a 2-liter crucible made of 404 stainless steel. The reduction process is conducted at a temperature of 750° C. in the presence of Sulfur Hexafluoride (SF_6) and CO_2 gases (e.g., shielding gasses).

[0079] To initiate the metallothermic reduction, 3.55 lbs. of magnesium is introduced into the crucible and melted at 675° C. Once the magnesium is completely liquefied, the melt temperature is raised to 750° C., and 0.8 lbs of calcium (Ca) is added. Halfway through the metallothermic reduction, an additional 0.24 lbs. of calcium is added, resulting in a total excess calcium of 70% by weight. To ensure uniform mixing, a piston-style mixer is employed, continuously moving the piston up and down in the crucible for a duration of 1 minute.

[0080] After 10 minutes of adding calcium, salt pucks comprising 84 wt. % $NdCl_3$, 8 wt. % NaCl, and 8 wt. % KCl are introduced into the metal melt mix. The temperature was maintained at 750° C. These salt pucks were used to maintain a low initial melting temperature and a low-temperature melting salt phase throughout the metallothermic reduction.

[0081] During the reaction, $NdCl_3$ reacts with Ca to produce neodymium (Nd) and calcium chloride ($CaCl_2$)). Due to the continuous formation of CaCl2, the composition and melting point of the system constantly changes. It should be noted that the salt phase is complex as the reaction involves the consumption of $NdCl_3$ and the formation of $CaCl_2$) in the presence of NaCl and KCl, resulting in a quaternary system mid-reaction.

[0082] After the addition of the salt pucks, manual mixing is performed using a piston mixer, with 3 pulls every 30 seconds. The reduction process was continued for approximately 2 hours. At the one-hour mark, an additional 0.24 lbs. of calcium was added and mixed at a temperature of 750° C. for another hour before concluding the reduction and casting the sample.

[0083] The resulting cast sample formed a magnesium alloy containing Nd and Ca. Analysis through inductively coupled plasma optical emission spectroscopy (ICP OES) revealed that the alloy contained 19.5 wt % Nd, thus representing 70% of the maximum Nd that could be reduced. However, the % total metal recovery is only 38% of the expected total metal. Correspondingly, the % Nd cast is measured at 26%.

[0084] Based on the assumption that the remaining metal phase is trapped in the high viscosity salt phase due to the formation of $CaCl_2$), additional steps were proposed to recover the trapped metal and improve the % Total Metal Recovered. Key findings from the reduction process include the successful reduction of $NdCl_3$ by Ca, the adverse effect of changing melting points in the salt phase on cast metal yield, and the necessity of using excess calcium for reduction.

Example B

[0085] In another non-limiting example, an improved method for metallothermic reduction results in the increasing the total metal recovered. The method incorporates additional steps to extract a larger portion of the total metal phase that is entrapped in the dense salt phase.

[0086] Similar to Example A, the reduction process involved the use of salt pucks comprising $NdCl_3$, NaCl, and KCl, with an approximate composition of 84 wt. % $NdCl_3$, 8 wt. % NaCl, and 8 wt. % KCl. The metallothermic reduction took place in a gas-fired furnace equipped with a 2-liter crucible made of 404 stainless steel. The metallothermic reduction was carried out at a reaction temperature of 750° C., with SF_6 and CO2 gases providing a controlled atmosphere.

[0087] In this example, 3.7 lbs. of magnesium was introduced into the crucible and melted at 675° C. Once fully liquefied, the melt temperature was raised to 750° C., and 1 lbs. of calcium (Ca) was added. By the end of the reduction process, a total of 90% excess Ca by weight had been added. To ensure thorough mixing, a piston-style mixer was utilized, which continuously moved the piston up and down in the crucible for a duration of 1 minute.

[0088] Ten minutes after the addition of Ca, the initial phase of the reaction was completed, and molten metal was cast. The resulting casting weighed 3 lbs. and contained 14.2 wt. % Nd, as determined by ICP OES. At this point in the method, approximately 60% of the Nd had been reduced, but only 37% of the Nd had been cast.

[0089] To initiate the second phase of the metallothermic reduction, 0.8 lbs. of NaCl/KCl salt pucks were added to the remaining salt slag and metal mix. These salt pucks consisted of 45 wt. % NaCl and 55 wt. % KCl and were intended to lower the melting point and viscosity of the salt slag.

[0090] After reducing the melting point and viscosity of the salt slag, an additional 3 lbs. of magnesium and 0.5 lbs. of calcium were added. The Ca addition marks the beginning of another hour of piston mixing, with 3 pulls every 30 seconds. Following this mixing period, the final phase of the reduction was completed, and the remaining metal was cast.

[0091] The resulting casting contained 3.5 wt. % Nd, as determined by ICP OES analysis. This represented an improved % Nd reduced of 64.3% as compared to the method in Example A. Furthermore, the overall % Nd cast was increased to 50.2%. This represented a 20% enhancement in % Nd cast and demonstrated the improved efficiency of the semicontinuous processing method.

[0092] The method of Example B allows for the recovery of a higher percentage of total metal by incorporating additional steps to extract metal trapped in the dense salt phase. The present disclosure represents a significant improvement over Example B, leading to higher overall efficiency in the metallothermic reduction process. FIG. **2** is a graph illustrated the relationship of the amount of Nd that is reduced in relationship to the amount of excess Ca added to the mixture. Referring now to FIG. **3**, there is illustrated one non-limiting process to produce rare earth metal Nd. As can be appreciated, other rare earth metals can be purified by use of the process illustrate in FIG. **3** and the in Examples A and B. As such, although the process illustrated in FIG. **3** begins with a rare earth oxide of Nd_2O_3, it will be appreciated that the process of FIG. **3** could alternatively or also have begun with other rare earth oxides (e.g., oxides of one or more of cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum, lutetium, praseodymium, promethium, scandium, ytterbium, and yttrium).

[0093] As illustrated in FIG. **3**, the rare earth chloride (e.g., $NdCl_3$, NdOCl, etc.) is prepared dry, and optionally in a vacuum, by the addition of NH_4Cl in excess to rare earth oxide.

[0094] In one non-limiting embodiment, the rare earth chloride (RE chloride) can optionally be formed as illustrated in Steps 1 and 2 of FIG. **3** by slowly heating the RE-oxide and NH_4Cl mixture in a vacuum so that the water byproduct can be drawn off to minimize or prevent the formation of RE-oxychloride. Optionally, the condensing of the NH_4Cl and water in a cold trap allows for recovery of the NH_4Cl. The formed RE chloride can be optionally vacuum dried. The vacuum drying process generally occurs at a temperature of 100° C.-200° C. (and all values and ranges therebetween), and typically about 130° C.-160° C.

[0095] In another non-limiting embodiment, the RE chloride can optionally be formed as illustrated in Steps 1 and 2 of FIG. **3** from digestion in HCL and addition of NH_4Cl, followed by boiling off free water to a controlled temperature below the oxychloride formation temperature, followed by optional vacuum drying. The vacuum drying process generally occurs at a temperature of 100-200° C. (and all values and ranges therebetween), and typically about 130-160° C.

[0096] After the formation of the RE chloride, alkali or other salts (e.g., [salts of lithium, sodium, potassium, rubidium, cesium], alkali metal hydroxides, sodium carbonate, alkali metasilicates, sodium carbonate, potassium carbonate, etc.) as illustrated in Step 3 of FIG. **3** can optionally be added to the RE chloride after the RE chloride has been optionally vacuum dried. The addition of alkali or other salts to the RE chloride is used to create a mixture with a melting point of no more than 1000° C. (e.g., 600-1000° C. and all values and ranges therebetween), typically no more than 850° C., and more typically no more than 800° C. The addition of alkali or other salts to the RE chloride can also be used to reduce the surface area and/or reduce the hydroscopic nature of the RE chloride.

[0097] After the optional addition of alkali or other salts to the RE chloride, the mixture can optionally be subjected to a high vacuum drying process (e.g., vacuum of less than 5 torr [e.g., 0.001-4.999 torr and all values and ranges therebetween], generally less than 1 or even less than 0.5 torr) at a temperature of 250-400° C. (and all values and ranges therebetween), and typically 300-350° C.

[0098] After the high vacuum drying process, the mixture can optionally be heated to the mixture melting point and then poured into ingots for later feeding and charging in the reaction vessel. As can be appreciated, the vacuum drying process, the high vacuum drying process, and the ingot forming process can be used on the RE chlorides that include or are absent the optional addition of alkali or other salts. The size and shape of the formed ingot is non-limiting.

[0099] Once the ingots that contain chlorides of rare earth metal are formed, the ingots are placed in the reaction vessel along with the addition of one of more metals and chloride salts as illustrated in Step 4 of FIG. **3**. The metals can be added in pure form, as a master alloy, and/or as a compound. The reaction vessel can be an iron vessel, a refractory metal vessel, a vessel that is coated with a refractory metal or ceramic material, etc.

[0100] After the rare earth metals or master alloys that include the rare earth metals are formed in the reaction vessel, the rare earth metals or master alloys that include the rare earth metals can optionally be further purified as illustrated in Step 5 of FIG. **3**.

[0101] Although example embodiments have been disclosed, a worker of ordinary skill in this art would recognize that certain modifications would come within the scope of the claims. For that reason, the following claims should be studied to determine their true scope and content.

[0102] It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained, and since certain changes may be made in the constructions set forth without departing from the spirit and scope of the disclosure, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense. The disclosure has been described with reference to preferred and alternate embodiments. Modifications and alterations will become apparent to those skilled in the art upon reading and understanding the detailed discussion of the disclosure provided herein. This disclosure is intended to include all such modifications and alterations insofar as they come within the scope of the present disclosure. It is also to be understood that the following claims are intended to cover all of the generic and specific features of the disclosure herein described and all statements of the scope of the disclosure which, as a matter of language, might be said to fall therebetween. The disclosure has been described with reference to the preferred embodiments. These and other modifications of the preferred embodiments, as well as other embodiments of the disclosure, will be obvious from the disclosure herein, whereby the foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims.

[0103] To aid the Patent Office and any readers of this application and any resulting patent in interpreting the claims appended hereto, applicants do not intend any of the appended claims or claim elements to invoke 35 U.S.C. 112(f) unless the words "means for" or "step for" are explicitly used in the particular claim.

What is claimed:

1. A process for producing rare earth metal (RE) or an alloy of rare earth metal (RE); said process is optionally a continuous or semi-continuous process; said process includes:

- a. adding to a reaction vessel an initial charge of a eutectic-forming metal that forms a eutectic with said RE; optionally adding calcium metal to said reaction vessel; said eutectic optionally has a metaling point of less than 1000° C.;
- b. adding to said reaction vessel an initial charge of anhydrous RE-chloride salt and/or RE-fluoride salt to form a charged mixture; optionally adding one or more alkali metal halides to said charged mixture; said charged mixture optionally has a melting point that is less than 1000° C.;
- c. heating said charged mixture in said reaction vessel; said temperature of said charged mixture in said reaction vessel is optionally greater than 700° C. and optionally less than 1000° C.;
- d. mixing said charged mixture in said reaction vessel to cause a reaction to convert the RE-chloride and/or RE-fluoride to RE metal and/or RE metal alloy and calcium chloride salt and/or calcium fluoride salt;
- e. removing a portion or all of the eutectic metal, rare earth metal, and/or rare earth alloy from said reaction vessel; optionally removing some or all of a salt mixture from said reaction vessel; and
- f. optionally adding additional eutectic-forming metal, alkali metal halides, calcium metal, RE-chloride salt and/or RE-fluoride salt to said reaction vessel, and then repeating the steps c-f to obtain additional amount of RE metal and/or RE metal alloy.

2. A method for producing rare earth metal (RE) or an alloy of rare earth metal (RE); said process is optionally a continuous or semi-continuous process; said process includes:

- a. providing a reaction vessel;
- b. providing a eutectic-forming metal;
- c. providing RE-chloride salt and/or RE-fluoride salt;
- d. providing a chloride and/or fluoride salt;
- e. adding said eutectic-forming metal, said RE-chloride salt and/or RE-fluoride salt, and said chloride and/or fluoride salt to said reaction vessel;
- f. causing said RE-chloride salt and/or RE-fluoride salt to react with other materials in said reaction vessel to form RE metal and/or RE metal alloy; and
- g. removing said RE metal and/or RE metal alloy from said reaction vessel.

3. The method as defined in claim **2**, including the step of adding calcium metal to the reaction vessel.

4. The method as defined in claim **3**, wherein said eutectic-forming metal is at least partially added as a master alloy that includes calcium.

5. The method as defined in claim **3**, wherein said eutectic-forming metal is melted in said reaction vessel prior to said addition of said calcium metal to said reaction vessel.

6. The method as defined in claim **2**, wherein said step of providing RE-chloride salt and/or RE-fluoride salt includes:

- i. providing Re oxide;
- ii providing a chloride and/or fluoride salt; optionally providing a chloride acid and/or a fluoride acid; optionally providing water;
- iii. mixing together said RE oxide, chloride and/or fluoride salt, optional chloride acid and/or a fluoride acid, and optional water to cause said RE oxide to form said RE-chloride salt and/or RE-fluoride salt; said step of mixing optionally occurring in a vacuum to remove water byproduct and inhibit formation of RE-oxychloride and/or RE-oxyflouride; said step of mixing optionally subjected to heating to remove water byproduct and inhibit formation of RE-oxychloride and/or RE-oxyflouride;
- iv. optionally condensing of chloride and/or fluoride salt and said water in an optional cold trap to recovery of said chloride and/or fluoride salt; and,
- v. optionally vacuum drying said formed RE-chloride salt and/or RE-fluoride salt; said vacuum drying optionally occurs at a temperature of 100° C.-200° C.

7. The method as defined in claim **2**, wherein said eutectic-forming metal includes aluminum, iron, magnesium, zinc, and/or aluminum.

8. The method as defined in claim **2**, wherein said RE-chloride salt and/or RE-fluoride salt is in the form of a pellet or ingot and optionally includes alkali salts.

9. The method as defined in claim **8**, wherein said pellet or ingot has a melting point of no more than 1000° C.

10. The method as defined in claim **2**, wherein i) said eutectic-forming metal, ii) said RE-chloride salt and/or RE-fluoride salt, iii) said chloride and/or fluoride salt, and iv) said optional calcium in said reaction vessel are heated to a temperature of no more than 1000° C.

11. The method as defined in claim **2**, further including the step of mixing and/or agitating i) said eutectic-forming metal, ii) said RE-chloride salt and/or RE-fluoride salt, iii) said chloride and/or fluoride salt, and iv) said optional calcium in said reaction vessel.

12. The method as defined in claim **2**, further including the step of adding alkali metal chlorides, alkali metal fluorides, calcium chloride, calcium fluoride, magnesium chloride, magnesium fluoride, metal halide chlorides, and/or metal halide fluorides to said reaction vessel.

13. The method as defined in claim **2**, wherein said RE-chloride salt and/or RE-fluoride salt is in the form of pellets or ingots.

14. The method as defined in claim **13**, wherein said pellets or ingots have a) a melting point of no more than 1000° C., b) a low surface area, and/or c) reduced moisture sensitivity.

15. The method as defined in claim **13**, wherein said alkali metal chlorides, alkali metal fluorides, calcium chloride, calcium fluoride, magnesium chloride, magnesium fluoride, metal halide chlorides, and/or metal halide fluorides are included in said pellets or ingots.

16. The method as defined in claim **2**, wherein said RE metal and/or RE metal alloy is allowed to separate from other materials in said reaction vessel prior to removal of said RE metal and/or RE metal alloy from said reaction vessel.

17. The method as defined in claim **16**, wherein a time for allowing said separation of said RE metal and/or RE metal alloy from other materials in said reaction vessel is at least 10 minutes, and optionally 10-60 minutes.

18. The method as defined in claim **2**, wherein said RE metal and/or RE metal alloy and any salt compounds in said reaction vessel are removed separately from said reaction vessel.

19. The method as defined in claim **2**, wherein said RE metal and/or RE metal alloy and any salt compounds in said reaction vessel are removed simultaneously, without separation, from said reaction vessel.

20. The method as defined in claim **2**, further including the step of i) purifying said RE metal and/or RE metal alloy and/or ii) separating said RE metal and/or RE metal alloy form said salt compounds; said step of purifying and/or separating optionally includes the use of a) centrifugal force, b) gas bubbling and/or c) distillation.

21. The method as defined in claim **2**, further including the step of adding sodium to said reaction vessel to at least partially regenerate calcium metal; said regeneration of said calcium metal optionally obtained in situ by a reduction of CaCl2.

22. The method as defined in claim **2**, wherein chloride salt and/or fluoride salt is at least partially removed from said reaction vessel is at least partially purified by partial crystallization of CaCl2 to within 10 degrees of the KCl—NaCl—CaCl2 eutectic.

23. The method as defined in claim **2**, further including the step of removing aluminum, iron, magnesium, zinc, and/or aluminum from said RE metal alloy; said step of removing aluminum, iron, magnesium, zinc, and/or aluminum from said RE metal alloy is optionally conducted with use of a multi-stage system; said multi-stage system optionally includes successively higher vacuum levels that draw on each successive evaporative chamber, and/or limited additional heat is added to each successive evaporative chamber to allow for recapture and reuse of latent heat during said removal process.

24. The method as defined in claim **23**, wherein a condenser of one of said chambers acts to provide a majority of heat for a successive evaporative chamber.

25. The method as defined in claim **23**, wherein said multi-stage system includes 3-6 evaporative chamber.

26. The method as defined in claim **2**, wherein no calcium metal is added to said reaction vessel; and any calcium in said reaction vessel is optionally formed by sodium additions to said reaction vessel which causes calcium-containing salts to react with said sodium and form calcium metal in said reaction vessel.

27. The method as defined in claim **2**, wherein some or all of said RE-chloride salt is replaced with RE-oxychloride salt and/or RE-oxyfluoride salt.

28. The method as defined in claim **2**, wherein said reaction vessel is at least partially formed of iron.

29. The method as defined in claim **2**, wherein said reaction of said RE-chloride salt and/or RE-fluoride salt in said reaction vessel occurs at a temperature of no more than 1000° C., and optionally no more than 850° C.

30. The method as defined in claim **2**, wherein said reaction vessel is partially or fully coated with a ceramic coating; said ceramic coating optionally including one or more materials selected from the group of yttrium oxide, zirconium oxide, calcium oxide, and magnesium oxide.

31. The method as defined in claim **2**, wherein a time of reaction of said RE-chloride salt and/or RE-fluoride salt in said reaction vessel is at least 5 minutes, and optionally about 5-30 minutes.

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