

Process for the recovery of lithium

The world consumption of lithium has more than doubled in the past decade. This increase is mainly due to its use in rechargeable lithium-ion batteries. Lithium-ion
5 batteries have indeed become the preferred source of electrical energy whenever high energy or high power is desired in applications where weight or volume are at a premium. This growth will likely continue in the next years: the global capacity of lithium-ion batteries that will hit the market each year is expected to reach hundreds of gigawatt-hours by the late 2020's.

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Different types of battery chemistries are in use, all of them based on the oxidation and reduction of lithium. Widely used cathode compounds include lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium nickel manganese cobalt oxide (NMC), lithium iron phosphate (LFP), and lithium nickel cobalt aluminum
15 oxide (NCA). At anode, lithium-graphite intercalation compounds are typical, with lithium metal or lithium titanate (LTO) also being developed. Lithium is furthermore used in the electrolyte in the form of LiPF_6 . The current lithium consumption in lithium-ion batteries accounts for about half of total lithium production.

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Lithium is also used in other products such as lithium primary batteries, as well as in lithium-bearing glasses, ceramics, polymers, casting powders, alloys, greases, and pharmaceuticals.

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From the above, it clearly appears that massive quantities of lithium will become available in all kinds of production scrap and in end-of-life goods. Recovery of that lithium may offer interesting industrial perspectives if efficient processes are developed.

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Up till now, the recycling of lithium from non-battery related materials has been fairly limited to the reworking of certain production scraps of the production process, like in the glass and ceramics industry. It is therefore expected that the future emphasis will lie with the recovery of lithium from lithium-ion batteries.

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Lithium-ion batteries involve complex compounds often comprising particularly valuable metals such as nickel and cobalt. The research in the field of battery

recycling has therefore been focusing on the recovery of these metals rather than on lithium. The literature describes several hydrometallurgical processes that use a variety of extraction and purification steps to recover nickel and cobalt from powders derived from lithium-ion battery waste. Lithium typically ends up diluted in the residual liquor of the last hydrometallurgical step. Often, this stream goes directly to the waste water treatment plant without any attempt to recover the lithium. In rare cases, lithium is nevertheless recovered by precipitation; this step generally offers only a low recovery yield, unless it is combined with an energy-intensive crystallization and evaporation step.

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As an alternative to a fully hydrometallurgical process, one could opt for a hybrid process comprising a pyrometallurgical first step. Pyrometallurgy has the notorious advantage of being robust and flexible with respect to the composition of the feed, from which specific elements can readily be concentrated in one of the metallurgical phases. Hence, from a lithium recycling perspective, a wide variety of lithium-containing scraps can be envisaged, including primary batteries, rechargeable batteries, glasses, ceramics, polymers, and casting powders.

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In the context of lithium-ion battery recycling, the recovery of lithium via pyrometallurgy has been described in "Valorisation of battery recycling slags" (Proceedings of the second international slag valorization symposium, pages 365-373, April 20th, 2011). Lithium is one of the most easily oxidized elements and is said to report to the slag. Subsequently, a hydrometallurgical process is described to recover the lithium from the slag. This is however a complex undertaking due to the dilution of the lithium in the slag, leading to diluted liquors containing marginally exploitable levels of lithium.

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The present invention solves this dilution problem by concentrating the lithium in the fumes of a smelting operation instead of in the slag. These fumes are formed in much smaller amounts compared to slag, thus offering a more interesting starting product for a hydrometallurgical process. The concentrated lithium fumes are moreover easily leachable, thereby facilitating the purification steps. This result is achieved by the addition of a suitable source of chlorides to the smelting furnace.

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It should be noted that the formation and fuming of lithium as LiCl, using CaCl₂ as a source of chlorides, has been described in the context of the lithium recovery from spodumene. A process has indeed been described wherein finely comminuted spodumene is mixed with powdered CaCl₂, the mixture being then subjected to high
5 temperature roasting in the solid phase.

Such a chlorination-roasting process is disclosed in US 2,561,439 and US 2,627,452.

10 US 2,561,439 teaches a vacuum chlorination-roasting process of comminuted spodumene pelletized with CaCl₂. LiCl evolves, which is condensed and recovered. US 2,627,452 teaches a preliminary thermal conversion of alfa to beta spodumene, followed by addition of CaCl₂, and by a second heat treatment in a rotary kiln, wherein LiCl is formed and volatilized.

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This chlorination-roasting process has also been applied to a lithium-bearing slag obtained from reducing smelting processes for the recovery of metals from spent lithium batteries. This is shown in CN 107964593 A, wherein the solidified lithium-bearing slag is first crushed and then mixed with a metal chloride such as CaCl₂.
20 Subsequently, the mixture is roasted, and the evolving LiCl captured. Such a multi-step process comprising the production of the slag via smelting, the solidification of the slag, its comminution, mixing it with fine CaCl₂, roasting of the mixture and capturing the LiCl is however both expensive and energy intensive.

25 In WO 2020/104164, good use is made of the fact that liquid phases are obtained during smelting, allowing for the combined recovery of valuable metals such as iron, copper, cobalt, and nickel in an alloy phase and of lithium in the fumes in a single operation. This process has a significant efficiency advantage since the slag does not need to be separated, mixed with a chloride source, and then re-heated to
30 perform the LiCl fuming.

On the other hand, this process creates large amount of waste materials, in particular chloride-containing waste in the form of salt discharge and increase in slag volume, which not only contributes to waste material, but negatively affects
35 nickel and cobalt yield. In addition, significant amounts of reagents are employed.

It was the objective to solve these problems with the process of the present patent application.

Thus, this patent application relates to a process for the concentration of lithium in metallurgical fumes, comprising the steps of:

- providing a metallurgical molten bath furnace;
 - preparing a metallurgical charge comprising lithium-bearing material, and fluxing agents;
 - smelting the metallurgical charge and fluxing agents in in said furnace, thereby obtaining a molten bath comprising a slag phase and optionally an alloy phase; and,
 - optionally separating the alloy and the slag phase;
 - fuming a major part of the lithium as Li halide from the molten slag, by addition of a halogen intermediate; wherein
- the process comprises at least one further step in which the halogen intermediate used for the fuming of Li halide from the molten slag is produced from the Li halide fumed from the molten slag, which is reacted under conditions sufficient to produce said halogen intermediate and a lithium product, and wherein halogen is selected from Cl, Br and I.

In other words, the patent application relates to a process for the concentration of lithium in metallurgical fumes, comprising the steps of:

- providing a metallurgical molten bath furnace;
- preparing a metallurgical charge comprising lithium-bearing material, and fluxing agents;
- smelting the metallurgical charge and fluxing agents in in said furnace, thereby obtaining a molten bath comprising a slag phase and optionally an alloy phase; and,
- optionally separating the alloy and the slag phase;
- fuming a major part of the lithium as Li halide from the molten slag, by addition of a first halogen intermediate;
- converting the Li halide fumed from the molten slag into a different lithium compound and a second halogen intermediate;
- re-using the second halogen intermediate in the step of fuming as first halogen intermediate;

wherein halogen is selected from Cl, Br and I.

The first and the second halogen intermediate do not need to have the same chemical form, as outlined further below. Key is, however, that the halide is advantageously re-used in the fuming step of the process.

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In order to both address the problems set out above and on top of that, simplify the process, it would be beneficial to employ a gaseous halogen intermediate.

Thus, another solution to the problem is a process for the concentration of lithium in metallurgical fumes, comprising the steps of:

- 10 - providing a metallurgical molten bath furnace;
- preparing a metallurgical charge comprising lithium-bearing material, and fluxing agents;
- smelting the metallurgical charge and fluxing agents in in said furnace, thereby obtaining a molten bath comprising a slag phase and optionally an alloy phase;
15 and,
- optionally separating the alloy and the slag phase;
- fuming a major part of the lithium as Li halide from the molten slag by addition of a halogen intermediate; wherein said halogen intermediate is a gaseous halogen or gaseous halogen compound, in particular a compound selected from a halogen or a
20 hydrogen halide, more specifically the halogen intermediate is selected from chlorine, bromine, iodine, hydrogen chloride, hydrogen bromide, hydrogen iodide and mixtures thereof. A most straightforward choice is chlorine, hydrogen chloride or mixtures thereof.

- 25 Obviously, a combination of the both solutions above might be advantageous as well, thus resulting in a process for the concentration of lithium in metallurgical fumes, comprising the steps of:
- providing a metallurgical molten bath furnace;
- preparing a metallurgical charge comprising lithium-bearing material, and fluxing
30 agents;
- smelting the metallurgical charge and fluxing agents in in said furnace, thereby obtaining a molten bath comprising a slag phase and optionally an alloy phase;
and,
- optionally separating the alloy and the slag phase;

- fuming a major part of the lithium as Li halide from the molten slag, by addition of a halogen intermediate; wherein
- said halogen intermediate comprises a gaseous halogen or gaseous halogen compound, in particular a compound selected from a halogen or a hydrogen halide;
- 5 and
- the process comprises at least one further step in which the halogen intermediate used for the fuming of Li halide from the molten slag is produced from the Li halide fumed from the molten slag, which is reacted under conditions sufficient to produce said halogen intermediate and a lithium product, and wherein halogen is selected
- 10 from Cl, Br and I.

More specifically, in this process the gaseous halogen or gaseous hydrogen halide is selected from chlorine, bromine, iodine, hydrogen chloride, hydrogen bromide, hydrogen iodide and mixtures thereof, with a straightforward choice being chlorine, hydrogen chloride or mixtures thereof.

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The addition of the halogen intermediate, more specifically of chlorides, leads to the fuming of LiCl and can be performed during or after smelting of the metallurgical charge. During the smelting the slag and the alloy are formed. It is also possible to perform the fuming on the molten slag, either before or after it has been separated

20 from the alloy, e.g. by tapping.

In an embodiment, the halogen intermediate may be fed to the furnace as part of the metallurgical charge, for example as part of the fluxing agents, or added separately to the liquid slag during or after smelting. If the halogen intermediate comprises a gaseous halogen or gaseous halogen compound it is advantageous if it

25 is added separately to the liquid slag during or after smelting.

The halogen intermediate may be an alkali halide, earth alkaline halide, a hydrogen halide, the halogen itself or combinations thereof. More specifically, the halogen intermediate may comprise calcium chloride and/or magnesium chloride, more

30 specifically the halogen intermediate may consist of calcium chloride, magnesium chloride or combinations thereof.

In another embodiment the halogen intermediate may comprise a gaseous halogen or hydrogen halide, more specifically the halogen intermediate may consist of

35 halogen or a hydrogen halide. In particular the halogen intermediate may comprise

chlorine or hydrogen chloride, more specifically the halogen intermediate may consist of chlorine or hydrogen chloride. The halogen might be combined with hydrogen, in particular in the absence of hydrogen halide.

Entry No.	First Halogen Intermediate	Second Halogen Intermediate	Other
1	Calcium Chloride	Chlorine	None
2	Calcium Chloride	Chlorine	Hydrogen
3	Calcium Chloride	Chlorine	Hydrogen Chloride
4	Calcium Chloride	Chlorine	Magnesium Chloride
5	Calcium Chloride	Hydrogen Chloride	None
6	Calcium Chloride	Hydrogen Chloride	Magnesium Chloride
7	Calcium Chloride	Chlorine	Hydrogen, Magnesium Chloride
8	Magnesium Chloride	Chlorine	None
9	Magnesium Chloride	Chlorine	Hydrogen
10	Magnesium Chloride	Chlorine	Hydrogen Chloride
11	Magnesium Chloride	Chlorine	Magnesium Chloride
12	Magnesium Chloride	Hydrogen Chloride	None

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After fuming the Li halide is being collected, for example by combining the fumes with a solvent, such as passing the fumes through a solvent or spraying water into the fumes, thus transferring the Li halide into a solution in a solvent or solvent mixture, particularly in water as the solvent.

10 Other possible means are common gas cleaning setups, such as using a scrubber for Li fumes.

By major part of the lithium is meant at least 50% by weight of the lithium entering the process.

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In this process, the metallurgical charge may comprise transition metals. The transition metals of most interest are iron, copper, nickel, and cobalt. Depending on the smelting and fuming conditions, the fumes may comprise, next to Li halide, one or more of the transition metals. Steps can be taken to remove these metals from

the Li halide, which in general can be done by conventional means such as keeping the pH of the solvent in the e.g. scrubber neutral. Transition metals can also be removed from the Li halide by crystallization or solvent extraction of Li, precipitating or solvent extraction of the transition metals.

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The process is particularly suitable for concentrating lithium present in materials also containing nickel and/or cobalt. A pO_2 is then maintained that is sufficiently low to reduce a major part of at least one of nickel and cobalt to the metallic state, allowing these elements to report to the alloy phase. pO_2 stands for partial pressure of oxygen. By major part is meant at least 50% by weight of the metals entering the process.

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The skilled person knows how to vary the redox potential by adjusting the ratio between oxidizing agents such as air or O_2 and reducing agents. Typical reducing agents are natural gas or coal, but could also be metallic fractions like aluminum, elemental carbon, and plastics present in the metallurgical charge. Most preferred, however, is hydrogen. Carbon can also be employed. The redox potential can be determined by monitoring the yield of the metals such as nickel and cobalt to the alloy.

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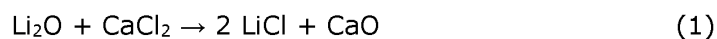
Lithium, which oxidizes easily, is assumed to quantitatively report to the slag. It will then react with the added chlorides, forming $LiCl$, which evaporates as fumes.

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The process is thus specially adapted for treating lithium-bearing materials comprising lithium batteries, their scrap, or their production waste.

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The stoichiometry of the chloride is determined according to the reactions:



in the case of $CaCl_2$ or $MgCl_2$ respectively.

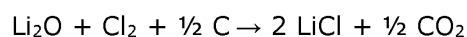
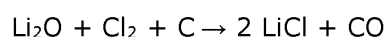
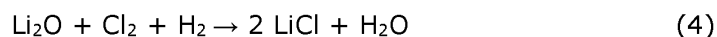
Other halides as well as halogen or hydrogen halides will undergo similar reactions with the lithium-bearing material.

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This might be improved by employing a reducing agent such as hydrogen (H_2) or carbon (C):

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- 5 In another embodiment a hydrogen halide such as HCl can be used, either alone or in combination with a halogen, such as chlorine. In this case hydrogen is not needed, which avoids the handling difficulties with this highly volatile and flammable gas. Use of a H₂/Cl₂ burner to both create heat and HCl can be a suitable approach.
- 10 As lithium is often used in batteries, in particular rechargeable batteries, the lithium-bearing material includes lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium nickel manganese cobalt oxide (NMC), lithium iron phosphate (LFP), and lithium nickel cobalt aluminum oxide (NCA) or other battery materials containing lithium. At anode, lithium-graphite intercalation compounds are typical,
- 15 with lithium metal or lithium titanate (LTO) also being developed. Lithium is furthermore used in the electrolyte in the form of LiPF₆. Lithium is also used in other products such as lithium primary batteries, as well as in lithium-bearing glasses, ceramics, polymers, casting powders, alloys, greases, slags and pharmaceuticals, which may also be present in the lithium-bearing materials. As
- 20 can be seen above, the lithium-bearing material may, for example, also contain nickel and/or cobalt.

In a specific embodiment, the lithium-bearing material comprises Li batteries, their scrap or their production waste.

- 25 In an embodiment the halogen intermediate is added in an amount corresponding to a stoichiometric excess with respect to the Li in the fumes. An excess stoichiometric amount of halogen intermediate helps in these reactions to come as close to a quantitative yield as possible. The amount of halide that is added should
- 30 thus preferably be at least stoichiometric with respect to lithium in the fumes. More preferably, a stoichiometric excess of more than 10 % is used.

When very high yields are desired, the amount of halogen intermediate is added should preferably be at least stoichiometric with respect to lithium in the slag. More

preferably, a stoichiometric excess of more than 10 % is used. This will usually ensure a lithium fuming yield of more than 80%, or even of more than 90%.

Suitable halogen intermediates are, for example, MgCl_2 , more preferably CaCl_2 .

5 These chlorides have a high boiling point of respectively 1412 °C and 1935 °C at normal pressure, guaranteeing a good availability of these chlorides to react with the oxidized lithium in the slag at the operating temperature of the smelting furnace. Another option with good availability is a halogen, hydrogen halide or mixtures thereof, in particular chlorine, hydrogen chloride and/or bromine,
10 hydrogen bromide and/or iodine and hydrogen iodide.

The Li halide, in particular lithium chloride, that reports to the fumes can be separated and collected from the flue gas by using common unit operations, like scrubbers, baghouse filters, electro-static precipitators and cyclones.

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The process described here comprises at least one step in which the halogen intermediate used for the fuming of Li halide from the molten slag is produced from the Li halide fumed from the molten slag, which is reacted under conditions sufficient to produce said halogen intermediate and a lithium product.

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This step in which the halogen intermediate used for the fuming of Li halide from the molten slag is produced from the Li halide fumed from the molten slag has the technical effect to make the halogen of the lithium halide available to be used in the fuming in the form of the halogen intermediate, thus reducing salt load, waste
25 materials and the need for adding expensive reagents.

In an embodiment the step in which the halogen intermediate is produced comprises an aqueous electrolysis step or a molten salt electrolysis.

30 The aqueous electrolysis step may comprise an electrolysis of an aqueous solution comprising the Li halide under conditions sufficient to obtain lithium hydroxide and the halogen intermediate that comprises hydrogen chloride, chlorine or mixtures thereof.

In an embodiment the step in which the halogen intermediate is produced
35 comprises a molten salt electrolysis.

The molten salt electrolysis comprises an electrolysis of a salt melt comprising the Li halide under conditions sufficient to obtain lithium metal and the halogen intermediate, in particular chlorine.

- 5 In another embodiment, the step in which the halogen intermediate is produced comprises
- an aqueous electrolysis and
 - optionally, a conversion reaction, in which the Li halide obtained from the fuming is converted into different lithium compound.

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More specifically, the aqueous electrolysis is an electrolysis of alkali halide to obtain alkali hydroxide and the halogen intermediate.

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Optionally, the alkaline hydroxide can be converted to alkali carbonate by reaction with carbon dioxide.

Said conversion reaction can be (a) a reaction of the Li halide with alkali hydroxide to alkali halide and lithium hydroxide, or (b) a reaction of the Li halide with an alkali carbonate to obtain lithium carbonate and alkali halide.

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Since Electrolysis often produces a halogen gas, more correctly a dihalogen gas such as chlorine gas (Cl_2), it can be combined with hydrogen to obtain hydrogen halide, such as, for example, hydrogen chloride (HCl) or other hydrogen halides like hydrogen bromide (HBr) or hydrogen iodide (HI).

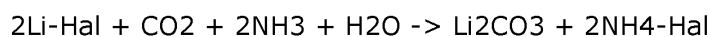
- 25 Both the halogen as well as the hydrogen halide gas, individually or in combination, are suitable as halogen intermediate. For example, chlorine or hydrogen chloride may be used as halogen intermediate as well as a mixture of chlorine with hydrogen chloride.

- 30 Consequently, alternatively to using gaseous compounds as halogen intermediate, the hydrogen halide can be reacted with alkaline or earth alkaline carbonates, hydrogen carbonates, oxides or hydroxides to form alkaline or earth alkaline halides that are suitable halogen intermediates, for example calcium chloride, magnesium chloride, sodium chloride or potassium chloride or other halides. Aluminum chloride
- 35 can also be useful as halogen intermediate.

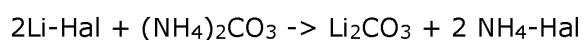
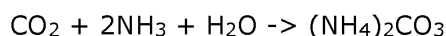
Other alkaline or earth alkaline carbonates, oxides, hydrogen carbonates or hydroxides of barium, strontium, rubidium and cesium are also suitable, but usually aren't economically feasible. Ammonium hydroxide or ammonium carbonate can
5 also be used instead of alkaline hydroxides or carbonates when appropriate.

One embodiment for converting the Li halide into the lithium product and the halogen intermediate is a reaction sequence similar to the Solvay process.

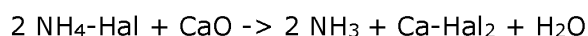
10 In this sequence, a concentrated solution of lithium halide is reacted with ammonia and carbon dioxide. This precipitates lithium carbonate, which is separated from the resulting ammonium halide solution.



Another option is to react ammonia and carbon dioxide upfront to produce
15 ammonium carbonate, and react lithium halide with the so produced ammonium carbonate



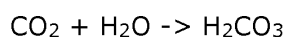
The ammonium halide can either be employed as halogen intermediate or reacted
20 with calcium oxide to regenerate ammonia, calcium halide and water to produce calcium halide as halogen intermediate.



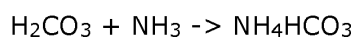
In this sequence, carbon dioxide is introduced into a concentrated lithium halide
25 solution together with ammonia. This precipitates lithium hydrogen carbonate, which is separated from the resulting ammonium chloride solution. Lithium halide reacts with carbon dioxide, ammonia and water to form lithium hydrogen carbonate and ammonium chloride ("sal ammoniac").

30 The individual partial steps:

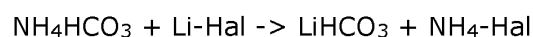
Carbon dioxide and water react to form carbonic acid



which in turn reacts with ammonia to form ammonium hydrogen carbonate



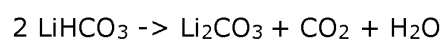
which in turn reacts with lithium halide to form the metastable lithium hydrogen carbonate and ammonium halide. When using Lithium chloride, ammonium chloride will be formed.



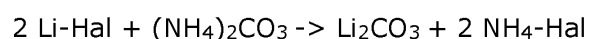
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If Lithium hydrogen carbonate is heated to approx. 95°C, whereby water and carbon dioxide are released, producing lithium carbonate as the lithium product. This can be accomplished by calcination. Dependent on the reaction temperature of ammonium hydrogen carbonate with lithium halide, lithium carbonate can be obtained directly.

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In another embodiment, lithium halide is reacted with ammonium carbonate, forming lithium carbonate directly.

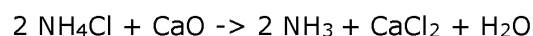


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Ammonium carbonate can be prepared by reaction of carbon dioxide and ammonia in aqueous solution:



20 In a subsequent step, the ammonia is recovered, which - analogous to the Solvay process - is used again in the reaction with carbonic acid to form ammonium hydrogen carbonate and can thus be reused.



The ammonium chloride can either be employed as halogen intermediate or reacted
25 with calcium oxide to form ammonia, calcium chloride and water to produce calcium chloride as halogen intermediate.

Example 1: Fuming with CaCl_2

End of life batteries with a composition according Table 1 are shredded to allow
30 easier manipulation and dosing.

A molten bath is then prepared in an alumina crucible of 2 L where 400 g of a starting slag is heated and melted in an induction furnace at a temperature of 1500 °C. This starting slag is the result of a previous operation and is used to provide a

liquid bath to which the batteries can be added. The composition of the slag is given in Table 2.

Once the slag is melted, the batteries are added together with limestone and sand
5 fluxes. The additions are made gradually over a period of 2 hours. During this time, O₂ is blown at a rate of 160 L/hour above the bath to combust the metallic Al and carbon present in the batteries.

After the final addition of battery scrap, CO is blown through the bath at a rate of
10 60 L/hour for 30 minutes to obtain a homogenous bath and fix the final reduction level. Samples of alloy and slag are taken. The mass balance of slag and alloy is shown in Table 2. The yields are calculated based on the alloy and slag phases only, thus discarding (minor) losses or carry-over to the gas phase.

15 Table 1: Composition of the batteries

	Al	Co	Cu	Ni	Li
Batteries (wt.%)	7	16	9	2,5	2,5

Table 2: Detailed material balance of the smelting operation before chloride addition

Input	Mass (g)	Al (wt.%)	Si (wt.%)	Ca (wt.%)	Co (wt.%)	Cu (wt.%)	Ni (wt.%)	Li (wt.%)
Starting slag	400	20	13	19	0,2	-	0,1	3,8
Batteries	1000	7	-	-	16	9	2,5	2,0
Limestone	300	-	2,2	38,0	-	-	-	-
Sand	100	-	46,7	-	-	-	-	-

Output	Mass (g)	Si (wt.%)	Ca (wt.%)	Co (wt.%)	Cu (wt.%)	Ni (wt.%)	Li (wt.%)	Al (wt.%)
Alloy	270	0,0	0,0	58,1	33,1	8,8	0,0	0,0
Slag	950	11,0	19,9	0,5	0,1	0,1	3,8	15,7

Yield	Mass (g)	Si (%)	Ca (%)	Co (%)	Cu (%)	Ni (%)	Li (%)	Al (%)
Alloy	22	0,0	0,0	97,2	99,0	94,6	0,0	0,0
Slag	78	100,0	100,0	2,8	1,0	5,4	100,0	100,0

5

While still at 1500 °C, argon is blown at a rate of 60 L/hour through the liquid bath to ensure mixing of the slag. From this experiment, it is clear that without the addition of chlorides, the Li remains in the slag.

- 10 Starting each time from the lithium-bearing slag according to above Table 2, 4 different experiments were performed, differing only in the total amount of CaCl_2 added. These 4 amounts represent 0%, 60%, 100% and 120% of the chloride needed for stoichiometric reaction with the Li present in the slag. CaCl_2 is added gradually during the first hours in 12 equal additions every 5 minutes. Prior to the
- 15 test the CaCl_2 is dried at a temperature of 150 °C in order to remove any water excess. The slag is allowed to react for an additional 30 minutes after the last CaCl_2 addition, while still continuing the gas blowing with Ar.

Samples of the slag are taken before the CaCl_2 addition, after the final addition, and 30 minutes after the last addition. The results are shown in Table 3, together with the overall yield of the Li to the fumes.

- 5
- For a sub-stoichiometric addition of 60%, all the CaCl_2 reacts with the Li in the slag to form volatile LiCl . A 100% stoichiometric amount of CaCl_2 is however not sufficient to vaporize the lithium quantitatively. A super-stoichiometric amount of 120%, equivalent to a 20% excess, achieves a lithium yield of 96%.
- 10
- Samples of the fumes all show a lithium concentration of 15%, which corresponds to a LiCl content of more than 90%. The remainder is primarily CaCl_2 present due to mechanical carry over.

Table 3: Li content of the slag in function of time and stoichiometry (CaCl_2)

CaCl_2	Li content in slag			Li yield to fumes
Stoichiometry	Before addition	After final addition	30 min after final addition	
0%	3.8	3.8	3.7	3%
60%	3.8	1.8	1.5	60%
100%	3.8	1.3	0.78	79%
120%	3.8	1.5	0.17	96%

- 15
- Similarly to the 4 experiments with CaCl_2 , 2 experiments were performed using MgCl_2 . The results are shown in Table 4. The lithium yields are markedly lower, though still satisfactory, in particular when using a 200% stoichiometry.

20 Table 4: Li content of the slag in function of time and stoichiometry (MgCl_2)

MgCl_2	Li content in slag			Li yield to fumes
Stoichiometry	Before addition	After final addition	30 min after final addition	
100%	3.8	2.2	1.9	51%
200%	3.8	1.0	0.8	78%

NaCl was also tested as chlorinating agent, resulting in a yield of 26% when using a 100% stoichiometry. A super-stoichiometric addition of 250% NaCl result in satisfactory yields of 50% or more. This is shown in Table 5.

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Table 5: Li content of the slag in function of time and stoichiometry (NaCl)

NaCl	Li content in slag			Li yield to fumes
Stoichiometry	Before addition	After final addition	30 min after final addition	
100%	3.8	3.0	2.8	26%
250%	3.8	2.1	1.8	53%

The CaCl₂, MgCl₂ and NaCl halogen intermediates can be obtained by converting the Cl₂ and H₂ gas produced during electrolysis to HCl and reacting the HCl with CaO, MgO and NaOH respectively.

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Example 2: Fuming with Cl₂

Starting from the lithium-bearing slag according to above Table 2, a new experiment is performed where 1 kg of the slag is kept at 1450°C while Cl₂ gas is blown through an Al₂O₃ tube submerged from the top into the liquid slag. The Cl₂ gas is generated during the electrolysis process. The gas is continuously blown for 120 min, so that after this 120 min, 1.6 times the stoichiometric amount of Cl is added compared to the Li in the slag.

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Samples of the slag are taken before the Cl₂ addition, and at different times during the experiments. The results are shown in Table 6, together with the overall yield of the Li to the fumes.

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Table 6: Li content of the slag in function of time and stoichiometry (Cl₂)

Cl ₂		
stoichiometry	Li content in slag (wt%)	Li yield to the fumes
0%	3,8	0%
50%	2,6	32%
100%	1,8	53%
160%	1,2	68%

Samples of the fumes all show a lithium concentration of 15%, which corresponds to a LiCl content of more than 90%.

- 5 Example 3: Fuming with HCl
- End of life batteries with a composition according Table 7 are shredded to allow easier manipulation and dosing.

10 A molten bath is then prepared in an alumina crucible of 2 L where 400 g of a starting slag is heated and melted in an induction furnace at a temperature of 1500 °C. This starting slag is the result of a previous operation and is used to provide a liquid bath to which the batteries can be added. The composition of the slag is given in Table 8.

15 Once the slag is melted, the batteries are added together with limestone and sand fluxes. The additions are made gradually over a period of 2 hours. During this time, O₂ is blown at a rate of 220 L/hour above the bath to combust the metallic Al and carbon present in the batteries.

20 After the final addition of battery scrap, CO is blown through the bath at a rate of 60 L/hour for 30 minutes to obtain a homogenous bath and fix the final reduction level. Samples of alloy and slag are taken. The mass balance of slag and alloy is shown in Table 8. The yields are calculated based on the alloy and slag phases only, thus discarding (minor) losses or carry-over to the gas phase.

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Table 7: Composition of the batteries

	Al	Mn	Co	Cu	Ni	Fe	Li
Batteries (wt.%)	7	2	2	9	15	2	3

Table 8: Detailed material balance of the smelting operation before chloride addition

Input	Mass (g)	Al (wt. %)	Si (wt. %)	Ca (wt. %)	Mn (wt. %)	Co (wt. %)	Cu (wt. %)	Ni (wt. %)	Fe (wt. %)	Li (wt. %)
Starting slag	400	20	13	19	6	0,2	0,2	0,1	0,1	3,8
Batteries	1000	7	-	-	2	2	9	15	2,5	3,0
Limestone	300	-	2,2	38,0		-	-	-		-
Sand	100	-	46,7	-		-	-	-		-

Output	Mass (g)	Si (wt. %)	Ca (wt. %)	Mn (wt. %)	Co (wt. %)	Cu (wt. %)	Ni (wt. %)	Fe (wt. %)	Li (wt. %)	Al (wt. %)
Alloy	270	0,0	0,0	0,1	7,3	32	55	5	0,0	0,0
Slag	956	10,9	19,8	4,6	0,2	0,2	0,1	1,5	4,7	13,7

Yield	Mass (g)	Si (%)	Ca (%)	Mn (%)	Co (%)	Cu (%)	Ni (%)	Fe (%)	Li (%)	Al (%)
Alloy	22	0,0	0,0	0,6	94,8	96,0	99,0	54,0	0,0	0,0
Slag	78	100,0	100,0	99,4	5,2	4,0	1,0	46,0	100,0	100,0

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While still at 1500 °C, argon is blown at a rate of 60 L/hour through the liquid bath to ensure mixing of the slag. From this experiment, it is clear that without the addition of chlorides, the Li remains in the slag.

- Starting from the lithium-bearing slag according to above Table 8, a new experiment is performed where 1 kg of the slag is kept at 1450°C while HCl gas is blown through an Al₂O₃ tube submerged from the top into the liquid slag. The HCl gas can be obtained by reacting the Cl₂ and H₂ gas from the electrolysis process. The gas is continuously blown for 120 min, so that after this 120 min, 1.6 times the stoichiometric amount of Cl is added compared to the Li in the slag.

Samples of the slag are taken before the HCl addition, and at different times during the experiments. The results are shown in Table 9, together with the overall yield of the Li to the fumes.

Table 9: Li content of the slag in function of time and stoichiometry (HCl)

HCl stoichiometry	Li content in slag (wt%)	Li yield to the fumes
0%	4,7	0%
30%	3,7	21%
60%	2,6	45%
90%	1,6	66%
120%	0,69	85%
140%	0,27	94%
160%	0,058	99%

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Example 4: Electrolysis of LiCl solution

The electrolysis setup comprised a membrane electrolysis cell with 100 cm² active membrane area. A stainless steel mesh cathode and an IrO₂-MMO anode were used.

- 10 A Nafion cation exchange membrane was placed between the anode and cathode compartment. Two bottles were connected to the anode and cathode compartments respectively and the electrolytes (anolyte and catholyte) were continuously circulated over the compartments with a flow rate of 200 mL/min using a peristaltic pump. The anolyte comprised 1 L of a 5 M LiCl solution. The catholyte comprised 300 mL of a
- 15 0.1 M LiOH solution.

A small amount of LiOH was initially added to the catholyte to ensure a minimal electrolyte conductivity. The electrolysis cell was connected to a power supply and a current of 2.5 A was applied, corresponding to a current density of 250 A/m².

- 20 The electrolysis process was performed at room temperature (21 °C) for 28 h. In Table 10, the volume and Li amount and concentration of the anolyte and catholyte before and after the experiment are indicated.

During the experiment, Li was transferred from the anolyte to the catholyte compartment and converted to LiOH. In addition to Li, also a part of the water was

25 transferred from the anolyte to the catholyte, which explains the decrease in anolyte volume and increase in catholyte volume.

A catholyte LiOH concentration of 4.6 M was achieved, corresponding to a current efficiency for Li of 72%. During the experiment, the formation of both Cl₂ and H₂ gas was demonstrated by gas analysis, which were re-used in the fuming reaction.

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Table 10 – LiCl electrolysis experiment (250 A/m², 21 °C, 28 h)

		Anolyte (LiCl)		Catholyte (LiOH)	
		Start	Stop	Start	Stop
V	mL	1000	870	300	420
Li	g	35.0	21.9	0.2	13.3
	g/L	35.0	25.2	0.7	31.7
	M	5.0	3.6	0.1	4.6

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Claims

1. Process for the concentration of lithium in metallurgical fumes, comprising the steps of:
 - 5 - providing a metallurgical molten bath furnace;
 - preparing a metallurgical charge comprising lithium-bearing material, and fluxing agents;
 - smelting the metallurgical charge and fluxing agents in in said furnace, thereby obtaining a molten bath comprising a slag phase and optionally an alloy phase;
 - 10 and,
 - optionally separating the alloy and the slag phase;
 - fuming a major part of the lithium as Li halide from the molten slag, by addition of a halogen intermediate; wherein
 - said halogen intermediate is a gaseous halogen, gaseous hydrogen halide or a
 - 15 combination thereof.
2. Process according to claims 1, wherein the halogen or hydrogen halide is added in an amount corresponding to a stoichiometric excess with respect to the Li in the fumes.
- 20 3. Process according to claim 2, wherein the stoichiometric excess of halogen or hydrogen halide amounts to at least 10%.
4. Process according to any of claims 1 to 3, wherein the halogen or hydrogen
25 halide is selected from chlorine, bromine, iodine, hydrogen chloride, hydrogen bromide, hydrogen iodide and mixtures thereof.
5. Process according to any of claims 1 to 4, wherein the process comprises at least one step in which the halogen intermediate used for the fuming of Li halide
30 from the molten slag is produced from the Li halide fumed from the molten slag, which is reacted under conditions sufficient to produce said halogen intermediate and a lithium product, and wherein halogen is selected from Cl, Br and I.
6. Process according to any one of claims 1 to 5, wherein the halogen
35 intermediate may further comprise alkali chloride, alkaline earth chloride or

combinations thereof, more specifically the halogen intermediate may further comprise AlCl_3 , MgCl_2 and/or CaCl_2 .

7. Process according to any one of claims 1 to 6, wherein the lithium-bearing
5 material also contains nickel and/or cobalt, and wherein a pO_2 is maintained that is sufficiently low to reduce a major part of at least one of nickel and cobalt to the alloy phase.

8. Process according to claim 7, wherein hydrogen, carbon or a combination
10 thereof is added.

9. Process according to any of claims 5 to 8, wherein the step in which the
halogen intermediate is produced comprises an aqueous electrolysis step or a
molten salt electrolysis.

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10. Process of claim 9, wherein the step in which the halogen intermediate is
produced comprises
- an aqueous electrolysis and
- a conversion reaction, in which the Li halide obtained from the fuming is
20 converted into different lithium compound.

11. Process of claim 10, wherein the conversion reaction is (a) a reaction of the
Li halide with alkali hydroxide to alkali halide and lithium hydroxide, or (b) a
reaction of the Li halide with an alkali carbonate to obtain lithium carbonate and
25 alkali halide.

12. Process according to any of claims 9 to 11, wherein the aqueous electrolysis
is an electrolysis of alkali halide to obtain alkali hydroxide and the halogen
intermediate.

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13. Process according to claim 9, wherein the molten salt electrolysis comprises
an electrolysis of a salt melt comprising the Li halide under conditions sufficient to
obtain lithium metal and the halogen intermediate, in particular chlorine.

14. Process according to claim 9, wherein the aqueous electrolysis step comprises an electrolysis of an aqueous solution comprising the Li halide under conditions sufficient to obtain lithium hydroxide and the halogen intermediate that comprises hydrogen chloride, chlorine or mixtures thereof.

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15. Process for the concentration of lithium in metallurgical fumes according to any of the preceding claims, comprising the steps of:

- providing a metallurgical molten bath furnace;
 - preparing a metallurgical charge comprising lithium-bearing material, and fluxing agents;
 - smelting the metallurgical charge and fluxing agents in in said furnace, thereby obtaining a molten bath comprising a slag phase and optionally an alloy phase; and,
 - optionally separating the alloy and the slag phase;
 - fuming a major part of the lithium as Li halide from the molten slag, by addition of a first halogen intermediate;
 - converting the Li halide fumed from the molten slag into a different lithium compound and a second halogen intermediate;
 - re-using the second halogen intermediate in the step of fuming as first halogen intermediate;
- wherein halogen is selected from Cl, Br and I, and wherein the first and second halogen intermediate comprise a gaseous halogen, gaseous hydrogen halide or a combination thereof.

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