

Toward Carbon-Negative Cement and Battery Materials

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Abstract. Decarbonization is the challenge of the century. Carbon-negative materials production and supply chains can be part of the solution. Negative Emissions Materials, Inc (NEM) has developed a process for production of carbon-negative nickel and cobalt battery material intermediates using a chloride based hydrometallurgical process route applied to saprolite ores. Amorphous silica, a supplementary cementitious material that can reduce the clinker content of cement mixes by 30%, is a coproduct. Magnesium hydroxide, a specialty chemical with several environmental applications, is the other major coproduct of the NEM process. The NEM process uses HCl leaching of saprolite to produce the silica residue, and the leachate is neutralized to produce an iron/aluminum/chromium residue as a potential coproduct. The iron-free solution is further neutralized to produce a mixed hydroxide precipitate (MHP) of nickel and cobalt followed by a high-purity magnesium hydroxide precipitate. The final solution is a concentrated sodium chloride solution which is directed to chlor-alkali processing to produce HCl and NaOH for acid leaching and neutralization. The process has advanced quickly through bench and pilot testing and is moving toward the development of the first large-scale demonstration plant. The process and the supporting testing will be presented.

Keywords: Carbon negative · Nickel · Cobalt · Hydrochloric acid · Sodium hydroxide · Chlor-alkali · Mixed hydroxide precipitation · Silica · Magnesium hydroxide

1 Introduction

1.1 Negative Emissions Materials

The Grantham Foundation for the Protection of the Environment leads their website with the statement “Climate change is the greatest challenge humanity has ever faced. It is the race of our lives.” All over the world we are seeing individuals, corporations, governments, and investors joining this race. The decarbonization of the transport sector is in full swing with accelerating uptake of electric and hydrogen powered vehicles. Power generation from wind and solar sources is increasing, and storage of electricity to stabilize grid power dependent on renewables is advancing. All of these efforts are making a difference as the race continues.

The demand for raw materials to enable many of the emerging transformative technologies is accelerating. Specifically, lithium, nickel, cobalt, and manganese are required for lithium ion battery manufacturing, and rare-earth elements are needed for electric vehicle traction motors and wind turbines. Further, when recovering critical raw materials for future use, the extraction industry must focus on zero waste production. All by-products/coproducts should be considered for use rather than storing in liquid or solid waste impoundments. Lastly, and perhaps most importantly, recovery of critical materials should be performed to produce a “carbon-negative” product, i.e., the best outcome would be to provide for future supply while creating pathways to remove carbon from the atmosphere.

Negative Emissions Materials (NEM) was founded to develop innovative technologies for critical materials supply, with by-products to enable an overall “carbon-negative” outcome. Technology development has focused on treatment of nickel saprolite ores, olivine, and asbestos tailings materials. These materials all contain magnesium silicate or magnesium hydroxy silicate minerals in addition to nickel, cobalt, iron, and other minor elements. The vision of NEM is to process these materials for nickel and cobalt battery material supply, silica product for material substitution in the cement industry, iron-containing precipitate for iron making or alternate use, and magnesium hydroxide. Magnesium hydroxide from the NEM process is carbon negative and may be used in the future to sequester atmospheric carbon dioxide using a variety of processes.

This paper is the first in a series of papers to report progress toward carbon-negative cement and battery materials.

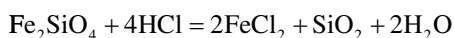
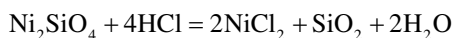
1.2 Process Flowsheet

The NEM general process flowsheet is shown in Fig. 1. The process involves the following:

Crushing and Grinding Crushing and grinding in recycle brine solution containing a variety of chloride salts, including magnesium chloride and sodium chloride. The purpose of recycle of a brine solution is to avoid the addition of water which can only be managed by evaporation which is expensive in terms of energy.

HCl Leaching This process uses HCl at high strength (typically 30–36% HCl by weight in water; a typical product from an HCl production facility attached to a chlor-alkali plant). The raw materials contain a variety of silicate minerals including magnesium, iron, nickel, cobalt, and minor impurity elements.

The chemistry therefore comprises the following major reactions:



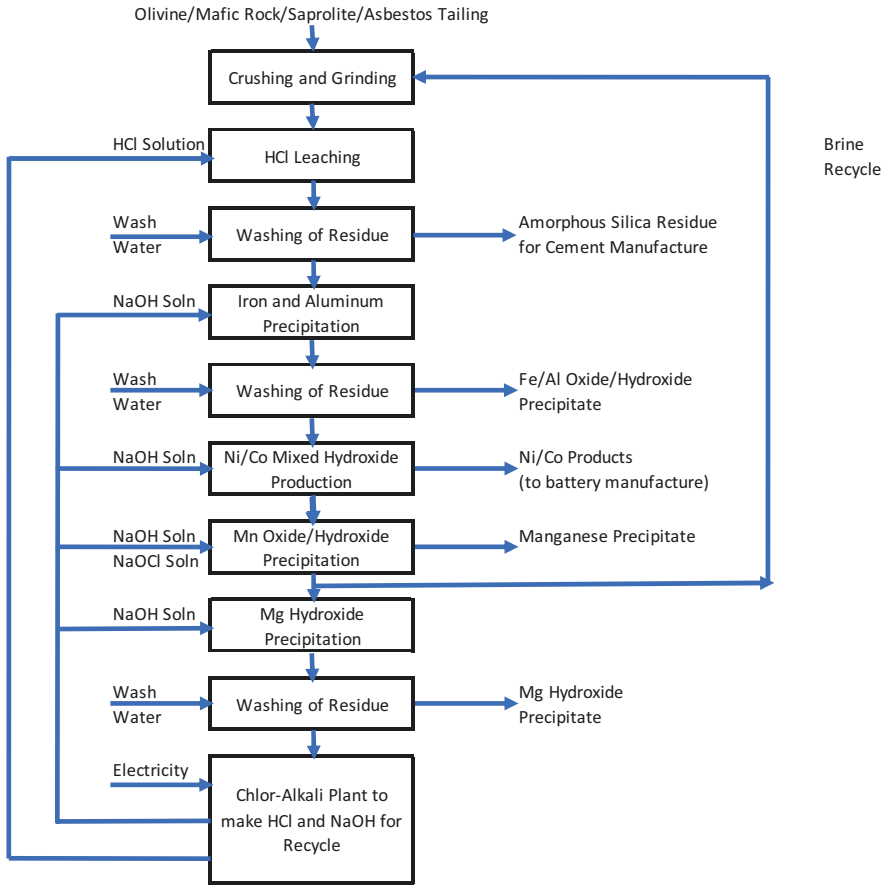
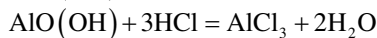
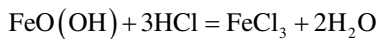


Fig. 1. The NEM simplified process flowsheet.

Note other minerals present such as iron oxides or aluminum oxides, may also react with HCl to form additional salts in solution.



Note that natural minerals are not pure compounds. The minerals may contain a variety of elements (e.g., Mg, Ni, Co, Fe in one silicate mineral) and may be hydrated or weathered. Suitable feed materials include the following:

- A. Nickel saprolite ores
- B. Olivine ores
- C. Asbestos ores and tailings.

The conditions for leaching are typically a temperature between 85 and 95 °C to the boiling point (probably 115 or even higher). Acid addition ranges from 500 to 1000 kg

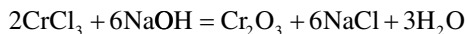
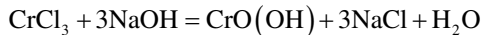
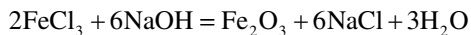
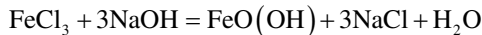
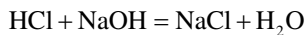
HCl per dry tonne of solid feed and will vary with the chemical composition of the feed. The brine recycle solution in the flowsheet below ensures that acid leaching is performed with a high total salt content as, for example, NaCl or MgCl₂ or both.

The leaching time can vary from 1 to 8 hours. The leaching can be done in a single-stage or two-stage countercurrent. Single stage means that the acid and ore are added together and allowed to react at temperature to completion, while two stage means that fresh ore is contacted with partly reacted solution so as to maximize the consumption of acid (low terminal acidity) and in the second stage, the partly leached ore (from the first stage) is contacted with high acid to maximize extraction of Mg/Ni/Co/Fe, etc. The two-stage process requires an additional solid/liquid separation step to ensure countercurrent movement of solids and liquids.

The products of HCl leaching are a weakly acidic solution containing various chloride salts and a silica-rich residue recovered as a solid product. This residue is washed to remove salts and excess acid with fresh water and then directed to cement manufacture where the silica is used as a replacement for other materials (thus lowering the carbon intensity of cement manufacture) and a strengthener to improve the yield strength of concrete (high-performance concrete).

Iron and Aluminum Removal The iron and aluminum content in the solution is precipitated as a mix of oxide and hydroxide solids by raising the pH with NaOH solution.

The NaOH solution is added as a 50% solution and may be diluted with recycle brine solution for process convenience and enhanced pH control (it may be difficult to control pH by adding such a strong base). The NaOH neutralizes the excess acid and precipitates Fe/Al and other trivalent cations if present, according to the following reactions:



The pH adjustment is conducted with stoichiometric amounts of NaOH. Over-addition will result in undesirable precipitation of Ni/Co, so careful control of addition must be maintained. The temperature will be 75 °C to the boiling point. Seed (precipitate) may be recycled to ensure growth of suitable sized particles for enhanced solid/liquid separation. Precipitation time can be 1–8 hours. NaOH is added progressively through the precipitation tanks (continuous) so as to enhance precipitation of coarser/separable precipitates. The product undergoes S/L separation and washing.

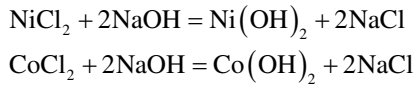
The iron/aluminum residue may be treated to form commercial products. This is a continuing program by NEM.

The iron and aluminum removal process can be performed in a two-stage arrangement to allow recycle of the second-stage precipitate to the leaching section to minimize any nickel and cobalt loss and to maximize the removal of iron, aluminum, and

chromium. Further, if the iron is partly in the ferrous state, a small amount of sodium hypochlorite may be added to oxidize residual ferrous to the ferric state.

Nickel and Cobalt Recovery Nickel and cobalt are present in solution as NiCl_2 and CoCl_2 salts. The recovery of Ni/Co can be done in many ways including the direct precipitation of mixed hydroxide precipitate (MHP). This can be done directly from the solution coming from the iron precipitation. Alternately ion exchange loading and elution with a bis-picolyamine resin can be used to recover an ion exchange eluant containing nickel and cobalt chloride at higher concentration.

In all cases, a solution of sodium hydroxide is added to form the precipitates.



Other metals will also precipitate with the Ni/Co in minor amounts, such as Mn and Fe (remaining iron in solution). If an excess of sodium hydroxide is added, then magnesium will co-precipitate as magnesium hydroxide. The selectivity of MHP precipitation can be enhanced by using two-stage MHP precipitation. The second-stage precipitate is recovered and recycled to the first stage or to the discharge from the main leaching step (where acid is present to redissolve the Ni/Co and other metals from the second-stage leach).

The mixed hydroxide precipitate is recovered by solid–liquid separation and washing. A pressure filter is often used with a “squeeze” cycle to minimize the entrained moisture in the washed MHP cake prior to shipping.

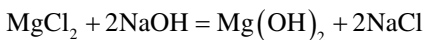
The precipitation is carried out between 25 and 90 °C and terminal pH is in the range of 5–8. Note that pH measurement is difficult in a strong salt solution, and sodium hydroxide addition can also be controlled by stoichiometry. The precipitation time is 1–8 hours. Seed recycling is used to maximize particle size and minimize contamination. The process (as in all steps) is conducted continuously.

Manganese Removal Manganese is an undesirable impurity in magnesium hydroxide, and cannot be selectively precipitated as a hydroxide in the presence of magnesium hydroxide. Accordingly, oxidation and precipitation are used to remove manganese from solution.



The manganese dioxide precipitate is filtered and washed.

Magnesium hydroxide precipitation The remaining magnesium in solution is precipitated by addition of NaOH to form $\text{Mg}(\text{OH})_2$.



This can be done by adding NaOH to MgCl_2 solution or by reversing the order of addition. The goal is to provide a near complete removal of Mg as $\text{Mg}(\text{OH})_2$ from solution, requiring a near stoichiometric addition of NaOH.

Chlor-Alkali Plant The final solution is NaCl and H₂O with some minor contaminants in solution. This solution is directed to a chlor-alkali plant for manufacture of NaOH, Cl₂, and H₂. This involves many steps. The Cl₂ and H₂ can be burned and water scrubbed to form strong HCl solution for recycle to leaching.

The excess heat from combustion is recovered as steam and used to evaporate excess water from solution.

2 Experimental Results

2.1 Raw Materials for Leaching

The three types of raw materials used in this study were obtained from various sources. Table 1 shows the elemental composition of the raw materials tested. The asbestos tailing was obtained from a tailing deposit in Quebec. Olivine (used as a foundry sand material) was provided by Essix Resources under the trade name Incast75. The nickel saprolite sample was provided by SGS Canada from an existing inventory of material.

The nickel and cobalt content of the material increases from asbestos tailing to olivine to nickel saprolite sample. Iron levels are variable from ~5% for the olivine sample up to 18% for the saprolite. The magnesium content was highest for olivine at 29.79% and only 12.2% for nickel saprolite. The silicon content varied over a narrow range of 15.6–19.49% Si. The samples were either used as received or ground to finer size as required.

2.2 HCl Leaching Test Results

A series of HCl leaching tests were performed to assess the extraction of the key elements (Ni/Co/Mg/Fe/Al) and the quality of silica residue produced as a product.

Table 1. Composition of raw materials for extraction.

Analysis (%)	Asbestos tailing	Olivine sample	Nickel saprolite sample
Ni	0.239	0.34	1.81
Co	0.011	0.011	0.052
Cu	0.0019	0.002	0.005
Zn	0.0019	0.004	0.02
Fe	7.51	5.13	18.0
Mg	22.2	29.79	12.2
Al	0.5	0.19	2.19
Cr	0.25	0.28	0.78
Mn	0.07	0.08	0.65
Ca	0.26	0.08	0.33
Si	16.5	19.49	15.6
Na	0.06	0.04	0.02
S	NA	NA	0.02

The leach extractions were highly sensitive to the acid addition, reported as kg HCl/tonne of material. The basis is kg HCl on a 100% basis and per tonne of dry ore (Fig. 2). The nickel extraction for the saprolite sample (Fig. 2) approached 100% at ~750 kg HCl/t of ore. Iron and magnesium extractions were slightly lower. It was technically feasible to produce $\geq 75\%$ SiO₂ content in the residue at the 750 kg HCl/t addition rate.

The olivine extraction results (Fig. 3) showed very similar extractions of Ni/Mg/Fe, consistent with the uniform mineralogy of the olivine sample. The acid required to reach maximum extraction was nearly 1200 kg HCl/t ore due to the more basic character of the olivine. The SiO₂ grade of the leach residue exceeded 80%.

The results of the leaching of asbestos tailings (Fig. 4) showed very high Ni/Mg/Fe extractions at +800 kg HCl/t. The SiO₂ grade again exceeded 80% in concert with high base metal extractions.

The batch leaching results showed that a variety of raw materials could be treated with suitable levels of HCl to maximal extraction of the key metals and production of a silica-rich residue.

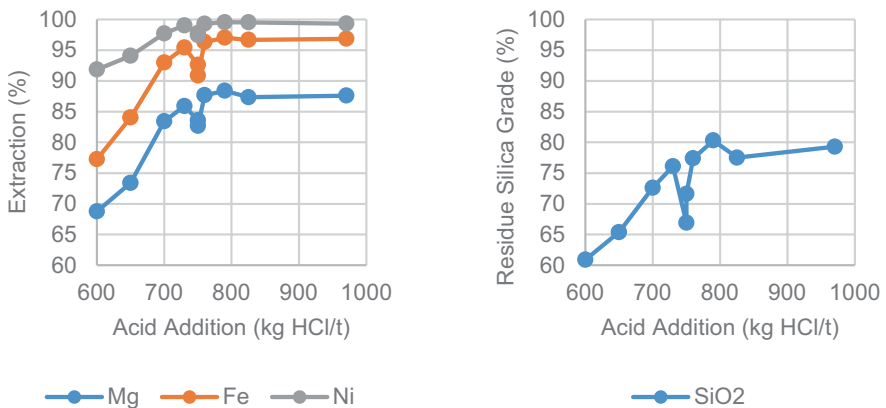


Fig. 2. Batch leaching results for saprolite. Typical conditions: Temperature 100 °C, 4 h, 87 g/L Mg (added as MgCl₂).

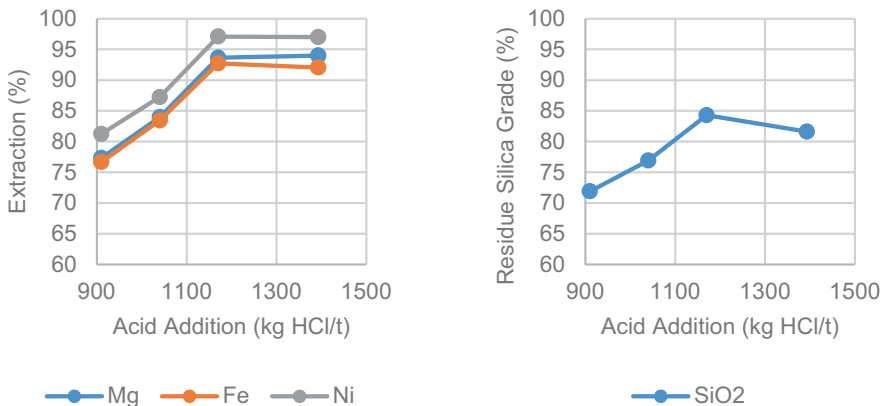


Fig. 3. Batch leaching results for olivine. Typical conditions: Temperature 100 °C, 4 h, 87 g/L Mg (added as MgCl₂).

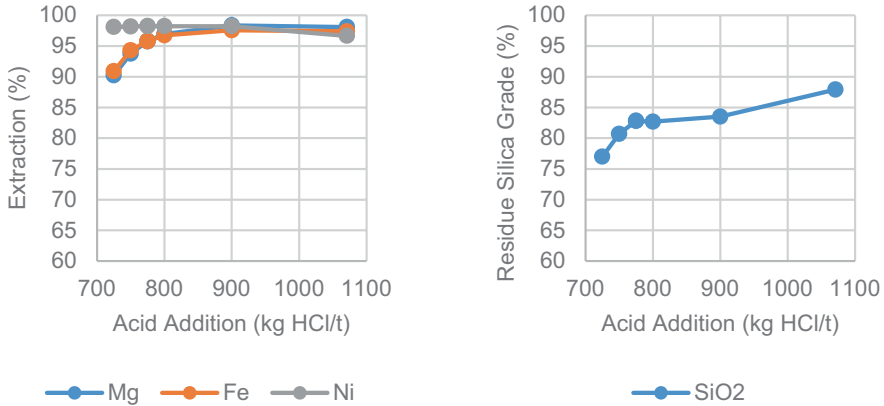


Fig. 4. Batch leaching results for asbestos tailings. Typical conditions: Temperature 100 °C, 4 h, 87 g/L Mg (added as $MgCl_2$).

2.3 Cementitious Properties of the Leach Residues

An extensive study of the cementitious properties of the leach residues was conducted. The results of this study will be reported in further publications. The leach residues containing high levels of residual silica were well suited to addition to cement.

2.4 Batch Testing of the Downstream Process Operations

In addition to an extensive series of batch leach tests, the downstream operations were also tested step by step in a series of further experiments. Table 2 shows the changing composition of solutions within the sequential unit operations in the NEM flowsheet applied to a nickel saprolite sample.

The leach solution contains over 3 g/L of Ni and high levels of Mg, Fe, and Al. The IR solution shows very low terminal Fe and Al concentrations and somewhat reduced Ni concentration, a consequence of some dilution due to base addition and some co-precipitation of Ni. The sodium level is increased due to NaOH addition, while manganese is diluted to 640 mg/L Mn in solution. The MHP (primary) solution shows very low Fe/Al and significant reduction in Ni. This experiment produced a high-grade MHP product (+40% Ni on a dry basis). The MnR solution shows an excellent rejection of Mn from solution (to 0.05 mg/L of Mn) by oxidation and pH adjustment. Further, the MP precipitation results show very low residual content of Mg, Ni, Fe, Al, and Mn. The final concentration of Na was 125 g/L Na, corresponding to 318 g/L NaCl. This brine would undergo further treatment in a conventional chlor-alkali circuit to polish minor contamination before electrolysis.

Table 2. Solution compositions (mg/L) through downstream unit operations.

Operation	Leach	IR	MHP	MnR	MP
Mg	69,600	63,000	68,800	62,300	3.1
Ni	3370	2210	300	1.7	0.6
Fe	36,900	3.6	0.3	0.2	0.5
Al	3470	10	0.2	0.2	0.2
Mn	750	640	630	0.05	0.05
Na	24	25,500	27,400	25,200	125,000
Test ID	SL2	IR5	MHP1	MnR3	MP5

Leach HCl Leach, *IR* iron removal, *MHP* mixed hydroxide precipitation, *MnR* manganese removal, *MP* magnesium hydroxide precipitation

2.5 Continuous Pilot Plant Results

A continuous pilot plant was established at SGS Canada to integrate the key elements of the process, from ground ore feed to the production of silica residue, iron/aluminum precipitate, mixed hydroxide of nickel and cobalt, manganese precipitate, and finally magnesium hydroxide precipitate. The barren solution after magnesium removal is also a product but in this case for recycle through a chlor-alkali facility for manufacture of sodium hydroxide and hydrochloric acid supply.

The pilot plant was run on a prepared sample of ground saprolite (Table 1) with grinding performed in recycle brine solution (Fig. 1). Leaching was performed with ~750–800 kg HCl/t feed material and 95 °C for 10 days total (two periods of 5 days). The leach slurry was collected and filtered in a pressure filter to recover the silica residue and the leach solution was directed to primary neutralization. A hematite-rich seed slurry was added to the feed solution as it entered four stages of neutralization with NaOH solution. The slurry product was thickened and the thickener UF was divided into seed recycle and final product. The primary neutralization thickener overflow was sent through secondary neutralization (four stages followed by thickening), where additional NaOH solution was added. The secondary neutralization thickener UF was recycled to leaching and the OF was directed to MHP production. MHP production was performed in two stages (primary and secondary), and the second-stage MHP thickener UF was recycled to leaching. The MHP thickener OF was sent to manganese removal. This was performed by oxidation with NaOCl and pH adjustment (with caustic addition) to form a manganese oxide product. Finally, the manganese-free filtrate advanced to magnesium hydroxide precipitation with sodium hydroxide addition (Fig. 5).

Saprolite Leaching The pilot plant operation was divided into 18 periods (each period was ~12 hours) over which data were collected and mass balances calculated. Figure 6 shows metal extraction versus time over these periods. The extraction of Ni in the saprolite leaching process was generally in the range of 96–99%. The Fe extraction was slightly lower and the Mg lower again. The acid addition rate was varied during the run and the changing extraction results are reflected by an increase or decrease in acid addition. The reported extractions are calculated by the Si-tie method where Si is assumed to be insoluble.

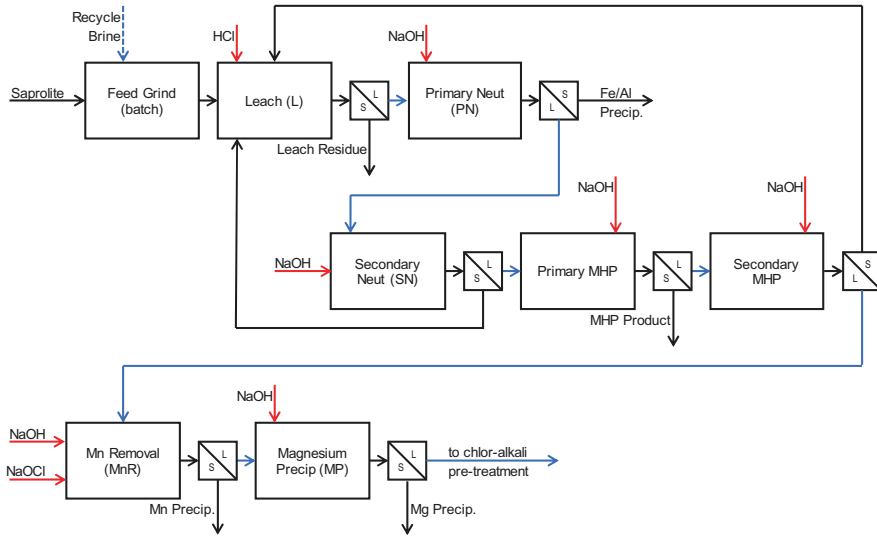


Fig. 5. Overall flowsheet of the continuous pilot plant.

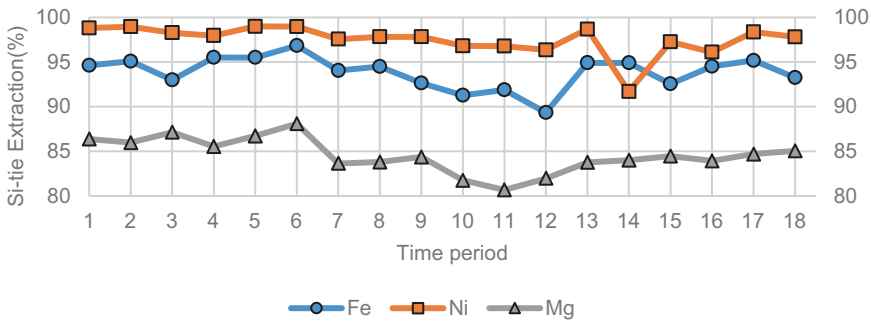


Fig. 6 Saprolite leaching results over the 18 time periods of the pilot plant operation.

Primary Neutralization The primary neutralization results are shown in Figs. 7 and 8. The iron removal results are consistent at nearly 100% efficiency. The aluminum removal results showed an increase toward the end of the pilot plant with a commensurate rise in nickel co-precipitation. The nickel in the primary neutralization residue is lost from the circuit, so better control is required to avoid a nickel loss while still removing sufficient aluminum in this step. Aluminum precipitation is an indicator of potential nickel loss. It is important to not over-add NaOH at this stage, otherwise nickel loss will increase. The solid assay from the primary neutralization circuit showed a plateau of approximately 80% Fe₂O₃ with 5.5% Al₂O₃ and 4% Cl. The iron and aluminum precipitates are hydrated and the chloride in the residue is likely due to formation of hydroxy chloride precipitates of iron and aluminum.

Secondary Neutralization The secondary neutralization results (Figs. 9 and 10) show excellent removal of iron and aluminum. However, if aluminum removal is too effi-

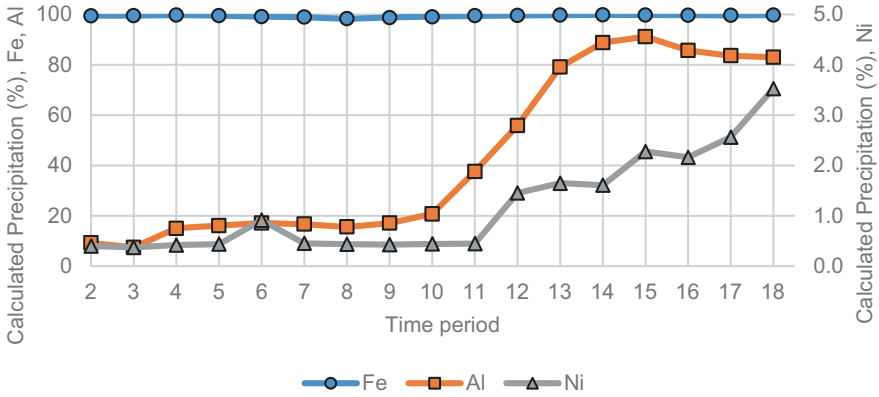


Fig. 7. Primary neutralization calculated precipitation.

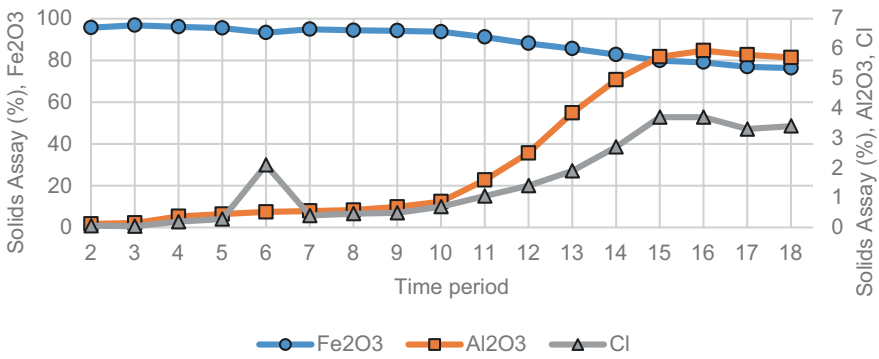


Fig. 8. Primary neutralization solids assay.

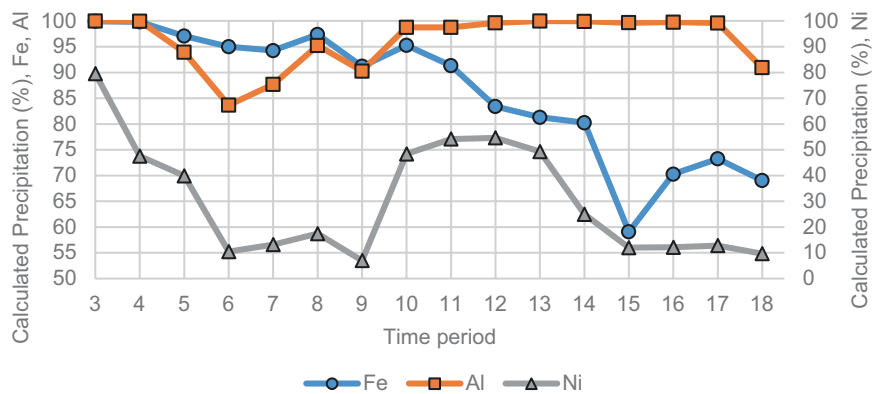


Fig. 9. Secondary neutralization precipitation efficiency.

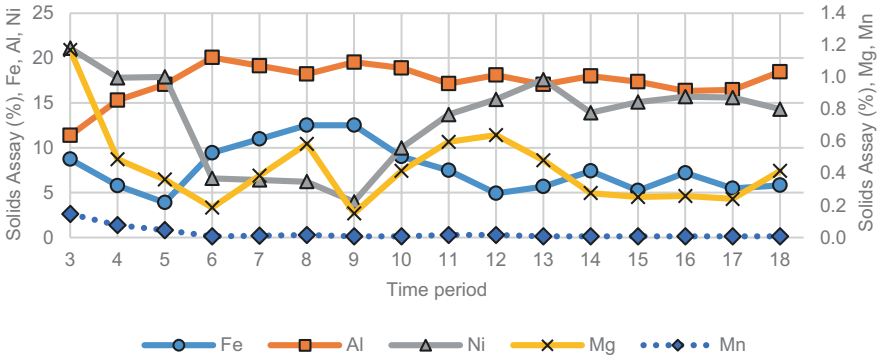


Fig. 10. Secondary neutralization solids assay.

cient, the precipitation of nickel increases. This is not a problem in the sense that the secondary neutralization residue is recycled and nickel is released. However, the nickel needs to move downstream to MHP precipitation, and therefore, nickel co-precipitation and aluminum removal have to be kept in balance to avoid excessive nickel buildup in the Leach Secondary Neutralization part of the circuit. This was an important learning from the pilot plant.

Primary and Secondary Mixed Hydroxide Precipitation The primary mixed hydroxide precipitation results (Figs. 11 and 12) showed that nickel could be precipitated to form high-grade MHP at as high as ~40% Ni on a dry basis (periods 5–8). The results also show the need for effective control of NaOH addition. During periods 9–18, excess NaOH was added, leading to increased precipitation of Mg and some Mn. The stability of this circuit is impacted by the upstream process steps and especially by the recycling of nickel and cobalt back to leach. Further, the measurement of pH in the strong brine solution as a measure of control is difficult and impacts the control of the MHP circuit. Future pilot plant operations will have improved pH electrode sensors and control.

The secondary mixed hydroxide precipitation results (Figs. 13 and 14) generally show the effective capture of residual nickel arriving from the primary mixed hydroxide circuit. Again the correct dosage and control of NaOH addition is a critical issue moving forward with the process scaleup. Under-addition of NaOH will result in loss of soluble Ni and Co to the manganese removal circuit, while over-addition will cause the precipitation of Mg and Mn.

Manganese Precipitation The manganese removal circuit (Figs. 15 and 16) was stable and yielded very high levels of manganese removal by effective oxidation and pH adjustment. Small levels of magnesium precipitation occurred through the operation, unavoidable due to the elevated pH used for manganese removal. The operation between period 5 and 10 showed some nickel in the manganese precipitate, due to incomplete nickel removal in the secondary mixed hydroxide precipitation circuit. Beyond this point (periods 11 and beyond), the nickel in solution in the feed to manganese precipitation was very low and, hence, the content of the manganese precipitate was very low.

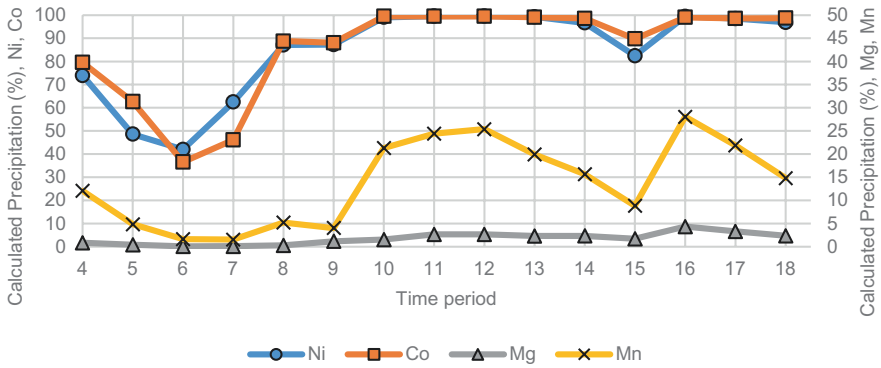


Fig. 11. Primary mixed hydroxide precipitation efficiency.

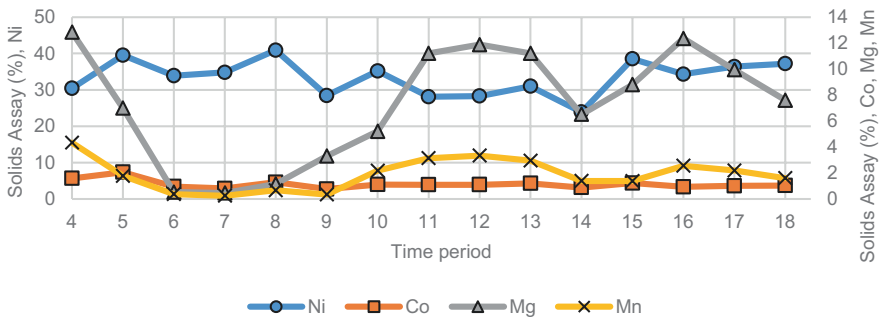


Fig. 12. Primary mixed hydroxide precipitation solid assay.

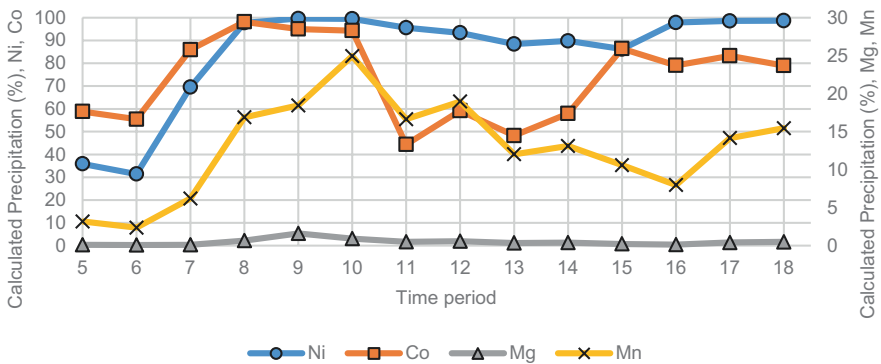


Fig. 13. Secondary mixed hydroxide precipitation efficiency.

Magnesium Precipitation The magnesium precipitation results were excellent (Table 3). The magnesium precipitation circuit operated toward the end of the 10-day pilot plant run. The key impurity elements were generally very low with the exception of chloride, which likely formed magnesium hydroxy chloride precipitates under startup conditions. Any of the other di- or trivalent metals present in the feed to magnesium precipitation will co-precipitate with the magnesium. Magnesium precipitation

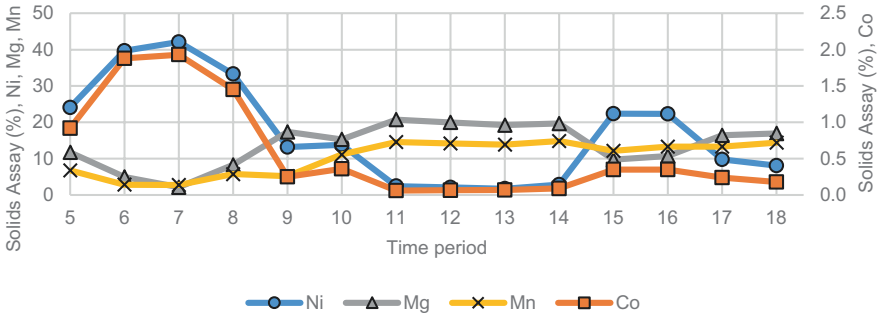


Fig. 14. Secondary mixed hydroxide precipitation solids assay.

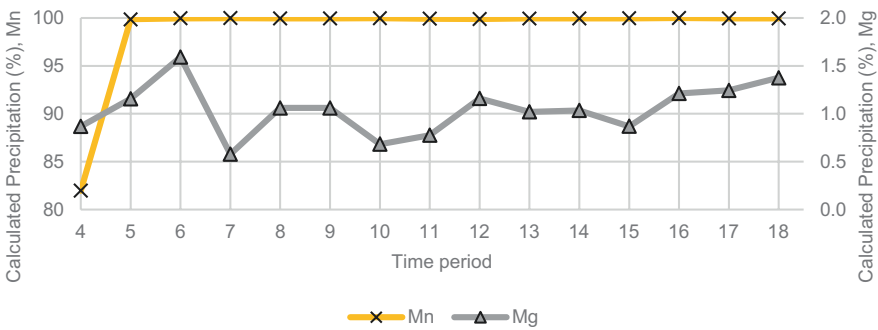


Fig. 15. Manganese precipitation efficiency.

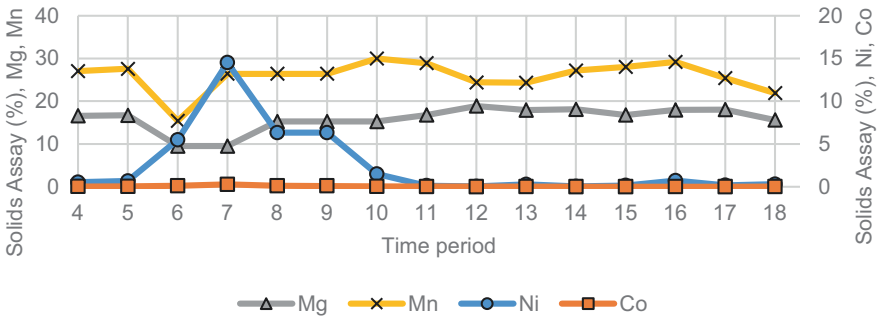


Fig. 16. Manganese precipitation solids assay.

Table 3. Magnesium precipitate analysis.

Chemical Analysis (%)							
Period	Fe	Al	Cl	Ni	Co	Mn	MgO
16	<0.01	0.02	4.4	<0.01	<0.01	<0.01	61.3
17	0.01	0.04	0.2	0.11	<0.01	0.01	63.1

efficiency was ~100%. The brine formed as a product from this process step is ideal as a feed to brine softening ahead of the chlor-alkali plant operation.

3 Conclusions

Following an extensive bench test program, the Negative Emissions Materials process was piloted on a sample of nickel saprolite ore for a total of 10 days. All the key metrics were achieved in the pilot plant operation:

- The leach extractions of nickel and cobalt were in the range of 96–99% in the primary HCl leach.
- The primary neutralization circuit removed iron and aluminum effectively with minimal co-precipitation of nickel and cobalt.
- The secondary neutralization circuit was effective at polishing residual iron and aluminum content from the solution prior to mixed hydroxide precipitation.
- The primary mixed hydroxide precipitation produced product grading up to 40% Ni on a dry basis. Under controlled conditions, co-precipitation of magnesium and manganese could be avoided. The testing highlighted the need to develop improved measurement of pH in the strong brine solutions used in this process so as to enhance control and selectivity of the key process steps.
- The secondary mixed hydroxide precipitation was effective at precipitating residual value metals.
- The manganese removal circuit utilizing oxidation and pH adjustment for precipitation was outstanding in performance with virtually 100% removal of manganese from solution.
- The magnesium precipitation process product was high grade and low in metallic impurities. The magnesium precipitation process is dependent on all of the upstream processes to produce a suitable precipitate product. The brine from the magnesium precipitation process was virtually free of any impurities and suitable as a source of NaCl brine to proceed to brine softening and chlor-alkali processing to regenerate HCl and NaOH for the process.

The silica leach residue from batch leaching of saprolite, olivine, and asbestos tailing was evaluated as an additive to cement. The results confirmed that the leach residues were reactive and suitable for cement making. The testing of the cementitious properties of the residue will be reported in a further publication.

The overall recovery of nickel and cobalt from the process is expected to be in the range of +95%. The MHP product is suitable for further post-processing to produce battery material precursor materials to support the rapidly increasing demand in the electric vehicle space. The magnesium hydroxide product from the process is an ideal material to support decarbonization. Future papers will provide further comment and data on this part of the work and process development.

Acknowledgments The authors thank the management of Negative Emissions Materials and SGS Canada for permission to publish this paper.