ENHANCING COBALT RECOVERY FROM COPPER/NICKEL MATTE PRODUCING SMELTERS

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ABSTRACT

Process Research ORTECH Inc. (PRO), with its in-depth knowledge on cobalt behaviour in nickel matte smelters and its novel mixed chloride hydrometallurgical processing, is developing a hybrid process to enhance cobalt recovery. PRO's experimental data is compared with plant information on cobalt behaviour in smelters. In final stages of iron rejection in the converters, the thermodynamics of the matte-slag system dictates the undesirable transfer of the cobalt to the final converter slags. This results in much lower cobalt recovery in the product Copper/Nickel matte (<60%) in present copper and nickel smelters. This information is used to transfer cobalt into desired quantity of converter slag. The enriched cobalt slag is subjected to PRO mixed chloride process to recover nickel, and cobalt as high value salts of importance in lithium ion batteries. From a typical converter slag containing 3.5% Ni, 1.5% Co, and 1.0% Cu, PRO leach process extracts 98 % Ni, and 98 % Co, and 99% Cu. Application of this process to enhance cobalt recovery in typical Copper/Nickel smelters is presented. In addition, this will also enhance the Copper and Nickel recovery. Both these aspects are of interest to the Copper, Nickel, and cobalt producers.

KEYWORDS

Atmospheric leaching, Cobalt, Copper, Mixed-chloride, Nickel

INTRODUCTION

In pyrometallurgical extraction of copper and nickel from sulphide ores cobalt often occurs with copper and nickel. The requirement of cobalt is increasing due to its need in lithium ion cells used in electric vehicles. Therefore its efficient and economical extraction in a form suitable for use in lithium batteries is of great interest at present.

In the pyrometallurgical processing of copper and nickel sulphide concentrates the concentrate is smelted to produce a furnace matte, which is then sent for converting to remove the iron to produce iron free (~1% Fe) matte for further processing to copper or nickel matte. The copper/nickel matte is processed for metals recovery by hydrometallurgical or vapo-metallurgical or oxidation – reduction routes to make market products.

As shown in Figures 1 and 2 the slags are produced in the smelting step and in the converting steps. The metal losses in smelting are controlled by the oxygen pressure in that step and slag production which is controlled by concentrate grade. The slag produced in the converting step which is carried out at a higher oxygen pressure contains higher level of metals is often returned to the smelting step to increase value metals recovery.

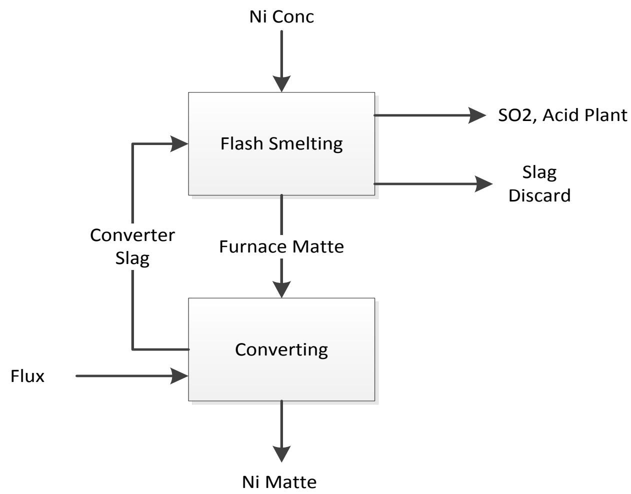

Figure 1. Nickel matte production by flash smelting at Vale Sudbury

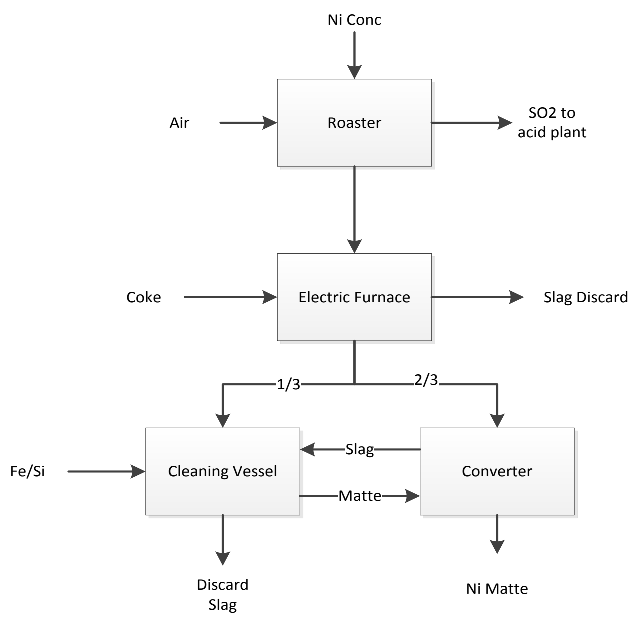

Figure 2. Nickel matte production by roast-reduction by Glencore at Sudbury

Sridhar and Toguri (1997 a,b) have studied the oxygen and sulphur pressures in copper smelting and are shown in Figure 3. The oxygen pressure in the smelting and converting is controlled by the activity of iron in the matte as per the following reaction.

$$Fe\ (matte)+1/2\ O_2\ (g)= FeO\ (slag) \qquad (1)$$

$$K = \frac{aFeO_{(slag)}}{aFe_{(matte)}} \times (p_{O_2})^{1/2} \qquad (2)$$

It can be seen that smelting occurs at an oxygen pressure of 10^{-9} atm to $10^{-10.5}$ atm. During converting the oxygen pressure is about 10^{-8} atm. The sulphur pressure is between 10^{-2} atm and $10^{-2.5}$ atm. Thermodynamics for nickel smelting is similar again controlled by iron.

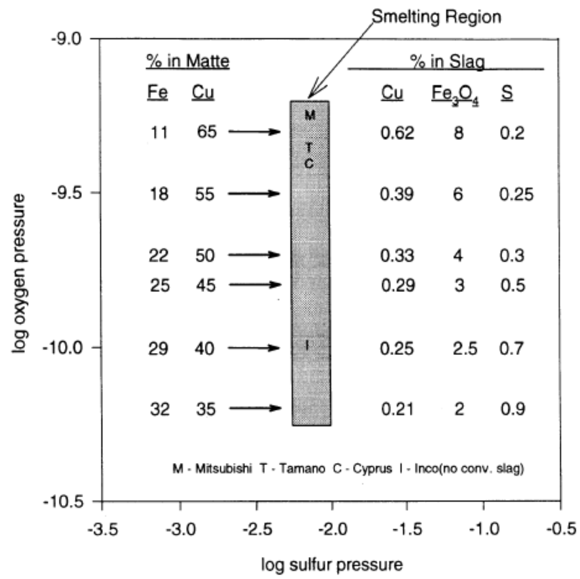

Figure 3. Copper smelting diagram (Sridhar et al., 1997b)

Figure 4 shows the free energy of the oxides of copper, nickel, cobalt and iron which is directly related to the oxygen pressure in the system. It can be seen that the iron is a reductant to oxides of copper, nickel and cobalt. Its oxide is most stable and its presence in matte reduces the copper, nickel, and cobalt from slag to recover these in the matte phase during smelting. It selectively oxidises during converting and enters the slag phase. At the end stages of converting when iron levels are low the cobalt oxidises followed by nickel and copper. Therefore by smelting at low oxygen pressures the recovery of copper, nickel and cobalt can be maximised and by converting the furnace matte to remove nearly all the iron especially the cobalt can be transferred to the slag from matte.

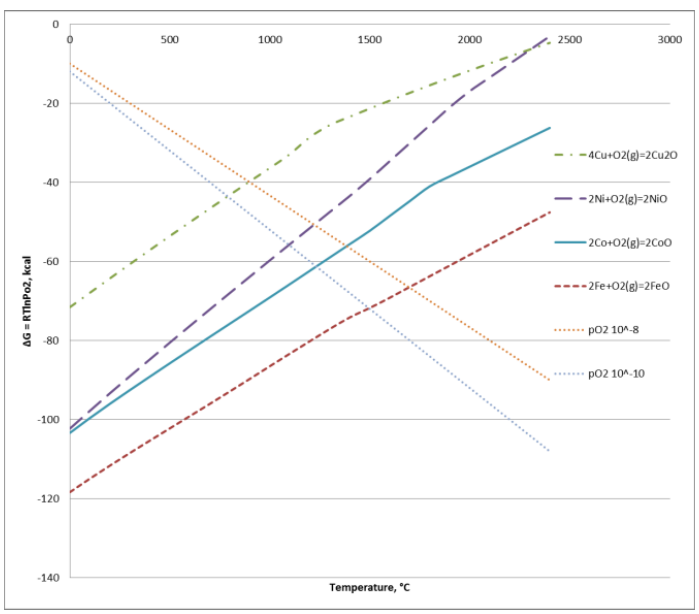

Figure 4. Free energy of formation of Cu, Ni Co and Fe oxides

PRO has developed a process to recover copper, cobalt and nickel from the slag into pure products. If converter slag with value metals, especially cobalt are subjected to the PRO process the overall metals recovery can be enhanced. The application of this process to enhance metals recovery especially cobalt is discussed.

COPPER AND NICKEL PARTITION IN SMELTING

The recovery of copper and Nickel in sulphide smelters are dependent on the copper and nickel partitions. The metals recovery can be derived from the metal partitions by the following formula:

$$\% \text{ metal recovery} = 100/(1+(\text{Ratio}*\text{metal partition})) \quad (3)$$

where metal partition is wt% metal in matte/wt % metal in slag and ratio is weight of slag/weight of matte.

In copper and nickel partition coefficients of 100 is targeted in plants and some plants have reported 150 for nickel partition.

With slag to matte ratios of 1 to 2 which is common in the smelters using optimum smelting and slag cleaning methods, the smelters target copper and nickel recoveries of over 97% with some reporting 98.5%. This is because iron is a good reductant especially for copper and nickel and is able to reduce the oxide present in the slag to metal in matte phase. On the other hand the oxide of cobalt is more stable and it is difficult to achieve such high partition coefficients.

In a laterite smelter making nickel matte product however the slag to matte ratio is about 12.5 and the nickel recovery into matte is only 94 % even with a high nickel partition of 175.

COBALT PARTITION

PRO has studied in depth the partition coefficients in the matte/fayalite slag systems and its results are shown in Figure 5. In this figure the mattes are what in metallurgical terms are called sulphur deficient. This is defined as mattes with sulphur less than that required to form FeS, Cu_2S, Ni_3S_2 and CoS. Detailed work at Inco and Falconbridge has shown that these systems give the highest partition coefficients for nickel and cobalt are achieved only with sulphur deficient matte and hence only these mattes are desired and considered here. In this figure data from plants are also shown. The agreement is fair and can be used to estimate the cobalt recovery during smelting and subsequent converting.

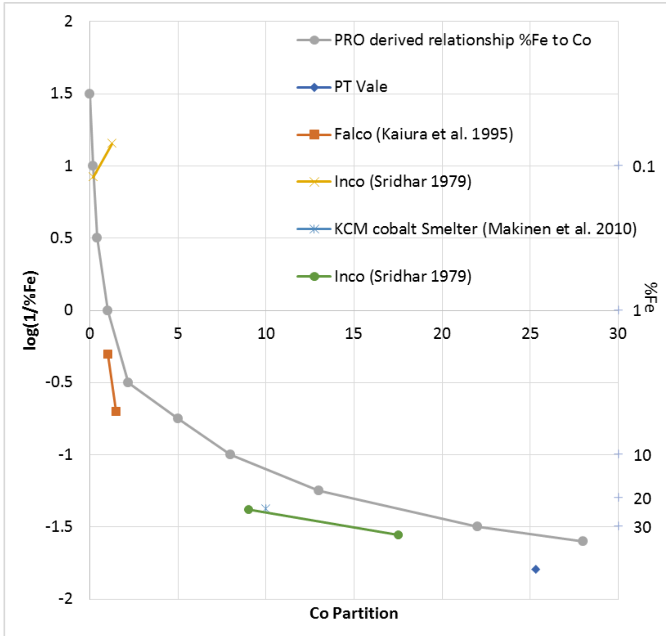

Figure 5. Derived relationship between iron and cobalt partition

PRO MIXED CHLORIDE PROCESS

PRO has developed mixed chloride process (Lakshmanan et al., 2014, 2018) to treat laterite ores and this has now been tested for converter slags from copper and nickel smelters. The flow sheet is shown in Figure 6.

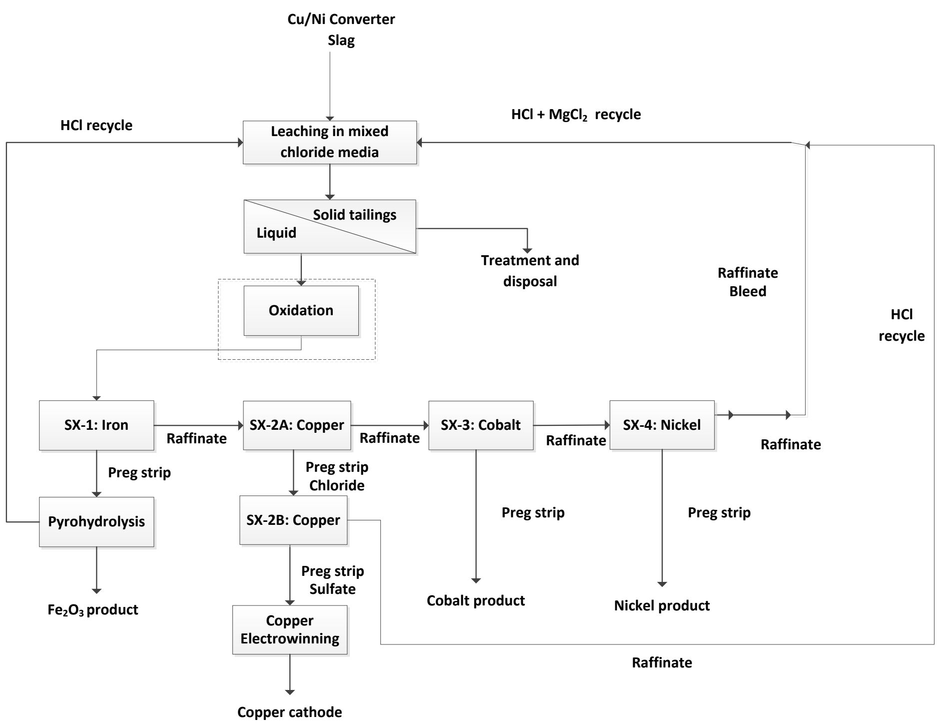

Figure 6. PRO flowsheet for treatment of Cu/Ni converter slag

The results for the PRO leaching of a nickel converter slag and copper converter slag are shown in Tables 1 and 2, respectively, where it can be seen that excellent recovery of value metals in the solution can be achieved. PRO has done extensive mini pilot plant studies on the solvent extraction and metals recovery by the PRO flowsheet. It has shown that high purity copper, nickel and cobalt streams can be produced from which desired salts of nickel and cobalt can be produced.

Table 1. Leaching of nickel converter slag with PRO mixed chloride

	wt.	Cu	Ni	Co	Fe	SiO2
				%		
Slag	100	1.03	3.53	1.56	49.85	25.00
Leach Residue	29.10	0.03	0.17	0.11	1.82	85.91
% Leach Extraction		98.98	98.84	98.43	98.98	0.00

Table 2. Leaching of copper converter slag with PRO mixed chloride

	wt.	Cu	Ni	Co	Fe2O3	Mo	SiO2
				%			
Slag	100	4.12	0.235	0.195	68.5	0.049	24.3
Leach Residue	30	0.12	0.0059	0.0056	2.7	0.029	82.4
% Leach Extraction		99.4	99.5	99.4	99.2	88.4	0

It has been possible to produce carbonate products of nickel and cobalt and also sulphate salts with Ni/Co ratio above 10,000/1 in the nickel product and above 10000 / 1 in Co/Ni in the cobalt product.

Though it is too early in the development process to get an accurate cost estimate, a preliminary CAPEX and OPEX for the process was developed. It has been estimated that OPEX costs are $100-120/t of slag and CAPEX costs of about $150/t of slag. As the metal values in the slag are high (>5% Ni + Co), the common method of looking at cost is as $/lb of product which results in an OPEX of ~$1/lb (Ni + Co) and a CAPEX of $10/lb (Ni + Co). This compares to an OPEX of ~$5/lb (Ni +Co) and a CAPEX of ~$100/lb (Ni +Co) reported for a commercial laterite plant. Therefore it appears very economical from the commercial point of view, however further development is required to confirm the OPEX and CAPEX estimate.

Salient features of PRO mixed chloride process:

1. Mixed chloride (HCl+MgCl2) enhances the activity of the H+ ions making the leach more efficient in the leaching step compared to HCl System
2. Leaching at atmospheric pressure at 70 to 95 °C.
3. Intermediate oxidation step may be required to convert ferrous iron (Fe^{2+}) to the ferric (Fe^{3+}) state for subsequent SX separation.
4. Higher chloride activity aids in some SX steps
5. Innovative separation of Fe from other metals in solution has been patented.
6. Innovative separation of nickel from other metals at high pH ~3 has been patented.
7. Developed methods to make sulphate products with high Ni/Co ratio and high Co/Ni ratio.
8. Recovers the iron, copper, nickel and cobalt from chloride solutions in the flowsheet and recycles the hydrogen chloride for leaching.
9. Iron oxide or metal is available as a by-product.
10. Enhanced recovery of copper, nickel and cobalt can be achieved from present smelter by using a hybrid system with PRO leach
11. The chloride systems are more friendly to silica containing slags with better solid-liquid separation and provide cleaner metal separations by SX route compared to sulphate systems.
12. The leach residue is essentially high grade Silica (~85%) which will be useful as high grade flux for smelting/converting lowering slag generation and lowering slag disposal requirements.
13. Preliminary economic estimates are favorable compared to conventional laterite processes.

POTENTIAL APPLICATIONS

Potential applications of this process to typical current operations are discussed here. In Canada two major operations using pyrometallurgical operations to recover nickel are located in Sudbury and the flow sheets used by the two companies Vale (old Inco) and Glencore (old Falconbridge) are shown in Figures 1 and 2.

Application to flash smelters

In the Vale plant in Sudbury, the smelting is done by flash smelting technology to make furnace matte. The furnace matte is then converted to eliminate iron to about 1% Fe and converter slag is returned to flash smelting furnace. In the flash smelting the oxygen pressure is high (about 10^{-8} atm) and the cobalt partition is about 6.

With the knowledge of cobalt partition and slag to matte ratio the cobalt recovery in the smelter can be calculated using the formula below:

$$\% \text{ Co recovery in matte} = 100 * (1/(1+ \text{Ratio}*\text{Co partition})) \quad (4)$$

where ratio is slag weight to matte weight ratio in the furnace vessel.

With a slag to matte ratio of about 2 the recovery of cobalt in flash furnace matte is about 75%. As seen in figure 4 during converting when iron in matte drops below 10% the cobalt partitions drop reaching about 1 at the end of the converter blow. Innovative methods of recycling high iron mattes etc. to different stages of converting or adding reductants such as FeSi are used to maximise cobalt. As matte with ~1% Fe is desired at the end of the converter blow, the overall cobalt recovery is less than what is desired in the current operation when making matte with 0% Fe. Earlier work of Sridhar et al. (1997 a) has shown that finishing at 5% Fe is beneficial but is often not desirable for downstream matte processing.

However cobalt that enters the slag especially during last stages is partly recovered when slag is returned to flash furnace. The result of such operation is the cobalt recovery achieved is low at 40 to 50%. In addition the cobalt value recovered in matte is not all recovered in products as some nickel products are sold with no value for the cobalt.

In the hybrid process discussed here it is beneficial to over blow the converter to less than 0.5%Fe in matte to transfer as much of the cobalt into the slag as possible in the last blow even with some nickel. This slag can be treated by PRO chloride leach to extract the nickel and cobalt very efficiently. As discussed above, the PRO leach has potential to recover more than 95% of the cobalt and nickel in the slag and the residue can be returned to converter/smelter as flux. With this method there is potential for the cobalt recovery in the smelter to be enhanced to over 70% from about 50% at present. With a production of 75,000 tpa of nickel this will be an enhanced production of over 500 tpa of cobalt in a saleable form in a Vale Sudbury type smelter.

Application to roast-reduction smelting

Diaz et al. (1994) have done extensive work at the Thompson smelter to optimise a roast reduction flow sheet to enhance both cobalt and nickel recoveries. They showed how cobalt partition of about 12 can be achieved in the smelting step compared to about 6 in flash smelting. This will relate to cobalt recovery of to about 86% for system with slag to matte ratio of 2. If this matte is converted to transfer cobalt to slag and treated by PRO process nearly all the cobalt in the slag can be recovered in the PRO process product and in the matte with very low iron (<0.5% Fe).

Application to Glencore Sudbury plant

Glencore plant operations (Stubina et al., 1994; Kaiura et al., 1995) at Sudbury the plant uses roast reduction smelting approach (figure 3) like the studies done at Thompson. In the plant further innovation of not returning the converter slag to smelting furnace to save energy and enhancing cobalt recovery is practiced. In the smelting stage with 2/1 ratio of slag to matte the recovery of cobalt will be about 86%. By various changes in treating converter matte and slag the cobalt recovery has been enhanced to above 60% in converter matte product.

If converting to ~0.5% Fe is done and the slag is treated by the PRO process there is potential to achieve cobalt recovery of over 80% from the PRO process products and in matte combined. With annual nickel production of 60,000 tons and a Ni/Co ratio in the concentrate of 25 this relates to added production of about 500 tpa of cobalt in saleable form. The PRO process will provide products suitable for lithium ion batteries which are desired by the market.

Application to PT Vale type flow sheet

With depletion of sulphide ore bodies the nickel producers are moving to laterite ore bodies. In Indonesia Vale operates a plant producing nickel matte by flowsheet shown in Figure 7.

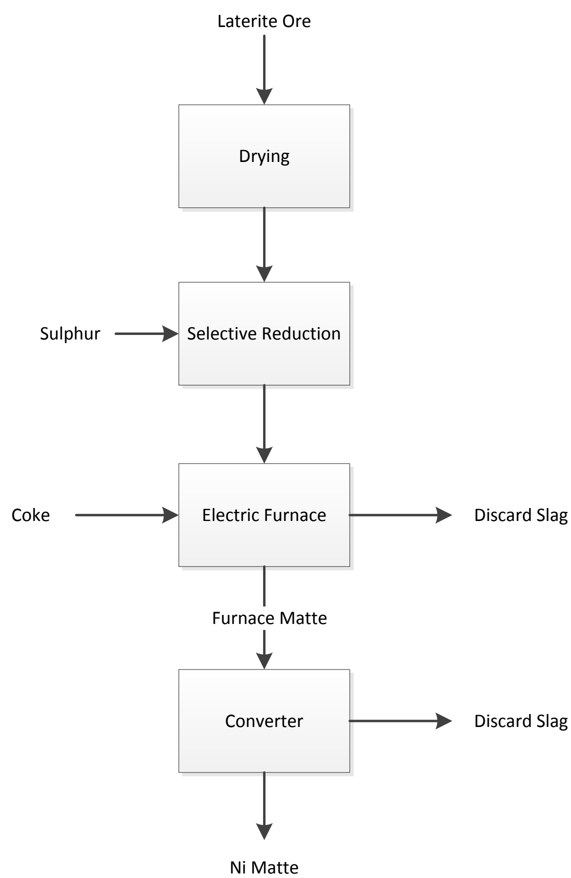

Figure 7. Vale laterite smelting process to make nickel matte

Typically in pyrometallurgical extraction of nickel from lateritic ore bodies the nickel is recovered in either the ferronickel or in matte form. In all smelters producing ferronickel the cobalt is lost as is of no value in the ferronickel. On the other hand if the Ni/Co ratio is less than 100 in ferronickel it is not desirable as the stainless steel product made from such nickel cannot go for nuclear application. As a result, PT Vale (formerly Inco) with a Ni/Co ratio of ~25 have adopted the matte flowsheet as shown in Figure 7. Reported recovery for the smelter is given in Table 3.

The cobalt is first recovered in furnace matte and then after conversion to remove iron, finished nickel matte goes for either refining where cobalt is recovered or is sold as a nickel product with no credit for cobalt.

Table 3. Typical furnace mass balance (per tonne of calcine) at PT Inco

Stream		Distribution	Ni %	Co %	Fe %	S %	SiO2 %	MgO %	S/M Ratio
Inputs	Calcine		2	0.08	19.4	1	39.9	20	2
Output	Matte	7.32	26.5	0.76	62.8	9.5			
	Slag	92.37	0.15	0.03	16.6	0.15	44.4	22.3	2
	Dust	0.31	2.5	0.06	20	1	39.5	12	3.3
Recovery	Matte		94.08	67.45	22.98	67.45	0.00	0.00	
	Slag		6.72	33.60	76.67	13.44	99.71	99.90	
	Dust		0.38	0.23	0.31	0.30	0.30	0.18	

The furnace matte containing 26.5% Ni, 0.76% Co and 62.5% Fe goes for conversion to remove iron. As seen in table the recovery of Ni and Co from the ore into the furnace matte is about 94% and 67.5% respectively. The reported matte composition after iron removal was reported to contain about 75% Ni and 0.8% Co which translates to a cobalt recovery of about 37% from furnace matte or about 26% from calcine. More recent assays reported in the financial reports indicates that matte now contains about 75% Ni and 1%Co which is likely due to improvements in the converter cycle and translates into a cobalt recovery of 46.5% in the converter and overall cobalt recovery of 31% from calcine.

Based on the cobalt partition information presented here and if the converter cycle is changed to transfer most of the cobalt in the final 25% of the converter slag and if that slag is treated by PRO leach the following is the estimated outcome.

1. The final matte will have lower cobalt of about 0.2 % and will lower loss in products like Tonimet.
2. The overall cobalt recovery to nickel matte and cobalt product from the PRO flowsheet will go up to about 50 % from 31% which for a plant producing 75,000 tpa of nickel matte will translate to a production of high value cobalt product from PRO process of about 1100 tpa. It is anticipated about 3300 tpa of nickel product suitable for lithium batteries will also be produced. The added cobalt recovery over current route is estimated to be about 600 tpa.
3. Another benefit will be about 1% higher recovery of nickel in the PRO nickel product as 25% of the converter slag will be treated and the contained nickel recovered.
4. Lowering of disposal of converter slag by 25%
5. High purity Iron oxide byproduct will be produced which is likely pay for the HCl regeneration cost in this process
6. Added benefit is about 25% of the converter silica flux will be regenerated and used in the converter process.

CONCLUSIONS

The above study shows the following:

1. The cobalt partition information presented here is in fair agreement with plant data and can be used to optimize cobalt recovery in smelters.
2. The final slags in nickel/copper converters with higher level of oxidation to make lower level of iron (<0.5%) will contain more cobalt than conventional converter slag.
3. If the above converter slag is treated by PRO mixed chloride flowsheet there is potential to recover more cobalt. This will also improve copper and nickel recoveries
4. The leach reside of PRO leach will be a high grade silica which can be recycled to converting and save disposal of about 25 to 100% of converter slag depending on tonnage processed by the PRO process.
5. With indications of potential increase of cobalt recovery of over 500 tpa in current operations this PRO hybrid route deserves a close examination for adoption.

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