

Sustainable Developments in the Nickel Recovery Process



John Quinn, Dennis Burger, and Shijie Wang

Abstract The conventional practice for controlling impurities and excess copper in the electrolyte at the copper refinery is to bleed a certain volume of electrolyte from the tankhouse and treat this bleed solution in a copper-removal circuit, i.e., deposit out or liberator cells. The decopperized electrolyte is then fed to the nickel sulfate plant, where crystallized nickel sulfate and black acid are produced from the evaporators. Aiming at sustainable developments, a new process to recover the nickel, was innovated and commercialized to eliminate the production of black acid and to cut the elevated energy cost at the FMI–El Paso Operations. This new environmentally friendly process is narratively described, viz., advanced decopperization, efficient recovery of sulfuric acid, effective removal of arsenic, antimony, and bismuth impurities, and economical recovery of nickel carbonate. Significant sustainable developments in the brown field, especially focusing on saving energy consumption and reduction of carbon dioxide (CO₂), are also rationally discussed in this paper.

Keywords Copper bleed electrolyte · Electrowinning · Acid purification unit · APU · Solution purification · Cathode copper · Sulfuric acid · Nickel carbonate

Introduction

To make electrolytic copper of commercially acceptable purity, both the concentration of impurities and of copper in the refinery electrolyte must be controlled. Conventional practice for impurity and copper control is to bleed a certain volume of electrolyte from the tankhouse and treat this bleed solution in a copper-removal circuit, i.e. liberator cells. The decopperized electrolyte is then fed to the nickel sulfate

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plant to control the concentration of nickel in the electrolyte. Currently, crystallized nickel sulfate is produced from evaporators and black acid, an environmentally hazardous waste, is generated from the process.

To reduce the waste of black acid and energy consumption in the evaporator operation of the nickel sulfate process, sulfuric acid has to be removed from the decopperized electrolyte and nickel sulfate in the spent electrolyte needs to be converted to nickel carbonate; which initiates a new scheme for treatment of tankhouse bleed electrolyte. After a literature review, Eco-Tec Technology [1], acid purification unit (APU), was innovatively developed in this experimental study to remove and recover sulfuric acid.

To produce a marketable nickel carbonate product, impurities in the bleed electrolyte, such as copper, arsenic, antimony, bismuth, iron, magnesium and zinc, have to be removed and the solution purified. Based on the differential solubility of base metals at different pH levels, chemical reagents, such as sodium carbonate (soda ash) and di-ammonium phosphate (DAP), are used in this experimental study to achieve the separation of the impurities and nickel carbonation in two filtration stages.

This paper covers the results of electrowinning pilot tests, APU ion exchange pilot tests, and the nickel carbonate plant commissioning for the tankhouse bleed electrolyte processing. An enterprise performance system, viz., understand customer requirements, innovate and employ the best processes, prioritize and leverage the actions you take to add value, and reduce waste and perform metal recovery friendly and efficiently, is also described for sustainable development in this paper.

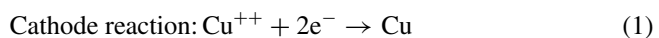
Process Description and Pilot Test Results

The process developed for the treatment of tankhouse bleed electrolyte is described under the headings of the important steps with the necessary process conditions and some reasons for their selection being included for each stage. A simplified process flow diagram is shown in Fig. 1. The major operations are:

- Removal of copper,
- Recovery of sulfuric acid,
- Weak acid solution purification,
- Recovery of nickel.

Removal of Copper

Electrowinning (EW) from tankhouse bleed electrolyte is a well-established technique for recovery of the copper. The electrowinning reactions may be described by the following general half reactions:



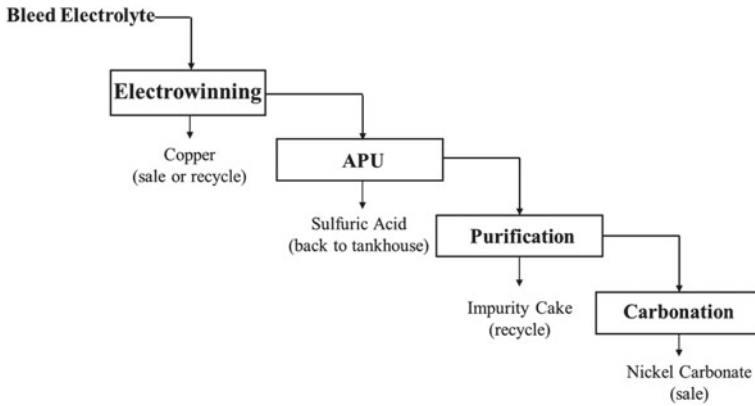
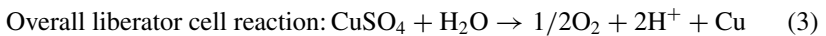
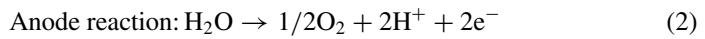


Fig. 1 A simplified process flow block diagram



The harvested copper cathodes can be either fed to rod casting or blended in anode casting in the plant.

For its bleeding, electrolyte is withdrawn from the electrorefining tanks and the copper is removed in the test cell (Fig. 2), using lead inert anodes and copper starting sheet cathodes. As shown in the table, the feed and final copper and sulfuric acid are 41.5 gpl and 4 gpl, and 194 gpl and 267 gpl, respectively. Good solid deposit with rough surface for recycle, while the final solution is sent to the APU pilot test for



Fig. 2 Copper removal pilot plant and EW test cell. (Color figure online)

Table 1 Operating data for EW pilot test

Customer solution: type volume	Tankhouse bleed (Cir. 5) 50 gallons	Cell data number type anode cathode		1 Rectangular 5 4			Pump: setting – 5gpm	
Date	Time	Rectifier output		Solution data				Notes
		Amps	Volts	Temp °F	Sample No EWP1–0	Cu C g	Acid gpl	
3/4	8:48AM							Start power on
	9:00AM	150	2.20	144	EWP1-0	14.5	194	
	2:30PM	150	1.90	144				
3/5	7:00AM	150	1.81	150	EWP1-1	39.8	210	
	4:00PM	150	1.81	150	EWP1-2			
3/6	7:00AM	150	1.90	145	EWP1-3	20.2	267	
3/6	12:15PM	150	1.90	135	EWP1-4	13.0	244	
3/6	4:00PM	150	2.00	130	EWP1-5	8.30	250	
	5:00PM	150	2.00	134	EWP1-6	4.00	267	
Avg./total	48 h	150	2.00	132				
			1.91	151				Shutdown havest

Copper cathode bottom sample chemical analysis:

Element: As Sb Te Bi Se Pb Fe Sn Ni Zn Mn Cd Si

ppm: 3.1 0.36 1.1 6 0.75 6.0 4.01.2 4.4 < 0.2 < 0.2 < 0.2 5.5

sulfuric acid recovery. A typical test analysis of the electrolyte for copper removal in the tankhouse and the copper cathode bottom sample are shown in Table 1.

Recovery of Sulfuric Acid

The low copper but high acid content solution is processed through the APU for recovery of sulfuric acid, which employs weak base ion exchange resins that have the ability to sorb acids while largely excluding metallic sulfates.

Copper cathode bottom sample chemical analysis:

Element As Sb Te Bi Se Pb Fe Sn Ni Zn Mn Cd Si ppm 3.1 0.36 1.1 63 0.75 6.0 4.0 1.2 4.4 < 0.2 < 0.2 < 0.2 5.5

The APU, originally developed at the University of Toronto and called Recoflo™, was introduced by Eco-Tec in 1977 for purification of sulfuric acid anodizing solution, which is characterized by the use of short beds and fine mesh ion exchange resins and operated in a counter-current flow scheme.

The APU is employed in the new process of treatment of tankhouse bleed electrolyte. The sulfuric acid that is recovered from APU can be used either as make-up acid in the stripper electrolyte in the tankhouse or in the autoclave leaching process at the Special Metals Plant.

Weak Acid Solution Purification

The weak acid solution from the APU pilot test (Fig. 3) is then purified by soda ash (sodium carbonate) and di-ammonium phosphate (DAP) for removal of impurities. These impurities must be removed so that a marketable nickel carbonate can be produced.

In both qualitative and quantitative chemical analysis, it is often necessary to take advantage of differing solubility to remove only one or several salts from solution. Calculations using solubility products can tell us when a separation of this type is possible.

Sodium carbonate (or soda ash) was chosen for pH adjustment rather than sodium hydroxide (or caustic) because it is cheaper. It was also chosen because the carbonate precipitate is a more granular material which is easier to filter. The dominant chemical reactions are given as follows, (at 25 °C):

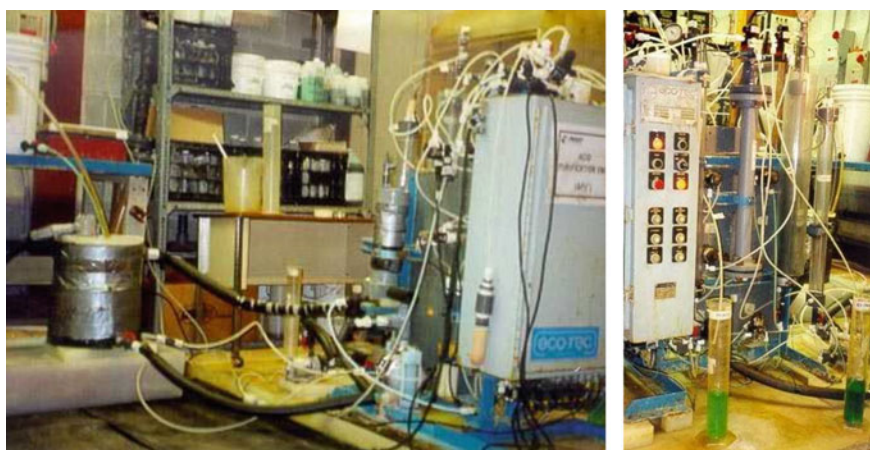
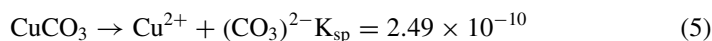
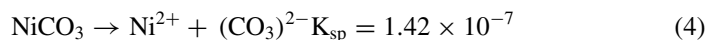
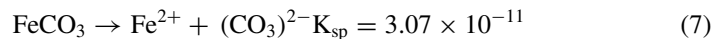
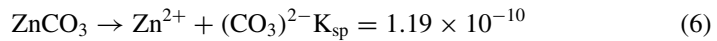


Fig. 3 Recovery of sulfuric acid pilot plant and APU test set up. (Color figure online)

Table 2 Effect of di-ammonium phosphate on impurities removal

Element	Di-Ammonium Phosphate			
	0	4.1	12.3	20.5
Ag (ppm)	<0.15	<0.15	<0.15	12
As (ppm)	0.6	17.8	34.2	53.6
Bi (ppm)	<0.2	<0.8	<0.8	<0.8
Ca (ppm)	114	109	86.1	84.8
Cr (ppm)	<0.15	<0.6	<0.6	<0.6
Cu (ppm)	408	472	148	179
Fe (ppm)	1	6.46	<0.2	0.62
Mg (ppm)	268	184	170	161
Ni (g/L)	15.8	13.7	11	9.5
Sb (ppm)	–	16	13.2	11.1
Se (ppm)	<0.25	<1.0	<1.0	<1.0
Te (ppm)	<0.4	<0.4	<0.4	<0.4
Zn (ppm)	221	200	75	66

^albs. DAP/lbs. dissolved impurity in the solution



The process makes use of the differential solubility of the above metals at different pH levels. Copper, iron and zinc can be partly removed from solution by an appropriate pH adjustment using sodium carbonate. The remaining impurities can then be selectively separated from the solution by adding DAP to precipitate the respective phosphates (Table 2).

Impurity salts are removed by filtration resulting in a filter cake that can be recycled to the smelter.

Recovery of Nickel

In the final step, the pH is raised to the optimum level of 9 by use of sodium carbonate (Fig. 4), causing precipitation of the remaining nickel, which is separated and recovered from the solution by filtration. The final solution (the filtrate) is sent to Tank 461 for water treatment in the Metal Recovery Plant.

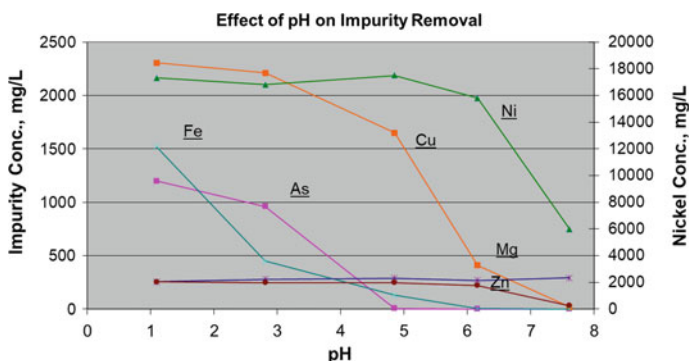


Fig. 4 Effect of pH for impurity removal. (Color figure online)

Innovative and Development Processes for Sustainable Development

New Environmentally Friendly Process

The old nickel sulfate plant removed the copper from tankhouse bleed electrolyte by electrowinning in the liberator cells. The decopperized solution was then evaporated and the nickel sulfate salts fell out of solution. Black acid, an environmentally hazardous waste, was simultaneously generated from the nickel sulfate process.

In order to eliminate the black acid and to stop the energy intensive evaporation, an innovative process was developed, viz., recovery of the sulfuric acid in an acid purification unit (APU), impurity removal by the selective precipitation, and recovery of the nickel through nickel carbonation reactors. The nickel sulfate plant was successfully transformed to the nickel carbonate plant, as shown in Fig. 5.

The process involves four major operations: removal of copper, recovery of sulfuric acid, removal of impurities, and recovery of nickel (Fig. 6). In the first stage, electrolyte is withdrawn from the electrorefining tanks in the tankhouse and the copper is removed in electrolytic cells using insoluble anodes and copper start sheets. The copper cathodes can be sold or recycled, and the copper-free solution is processed through the second stage that employs weak base ion-exchange resins that have the ability to absorb acids while largely excluding metallic sulfates. The sulfuric acid that is recovered is used as make-up acid in the stripper electrolyte in the tankhouse. The sulfuric-acid-free solution is then treated in the purification circuit (the third stage), where a residue containing arsenic, antimony, bismuth, etc., is removed. In the final stage, the purified nickel sulfate solution is processed and the nickel carbonate is separated and recovered from the solution by filtration. The final solution (the filtrate) is sent to the water recovery plant.



Fig. 5 Nickel carbonate plant—filtration-APU-purification-carbonation. (Color figure online)

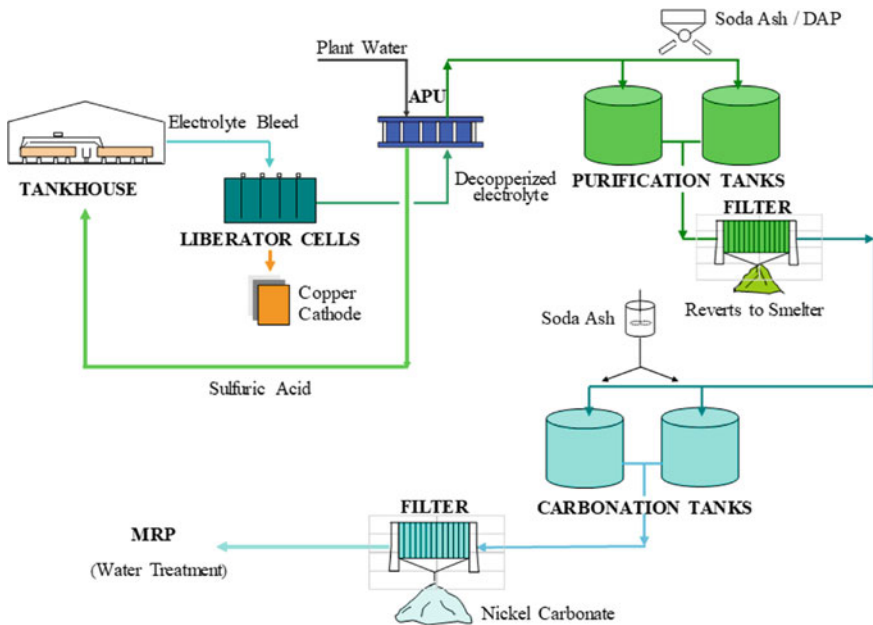


Fig. 6 Treatment of tankhouse bleed electrolyte. (Color figure online)

Nickel Carbonate Plant Engineering and Commission

A research report [2] titled “A new process development for treatment of tankhouse bleed electrolyte” was submitted in August 2002. Based on the successful nature of the results obtained, a preliminary economic evaluation was made on the promise of treating 5000 gal/day of tankhouse bleed electrolyte.

Primarily due to the elimination of black acid, evaporator operation and the recycled sulfuric acid, the financial benefits were found to be attractive. Results of the economic evaluation were summarized, process and financial bases and assumptions for the proposed commercial operation were then presented to the senior management for approval.

Based on the substantial environmental and economic benefits which would be provided by the process, the APU project was approved and the engineering report was later finished and submitted in November 2003. The Nickel Carbonate Plant was designed and the construction and equipment installation were finished by June 2004. The APU and Nickel Carbonation and the NCP commissioning were then carried out in sequence and finished in early August 2004.

With the new process, black acid is eliminated. Since nickel is recovered as a nickel carbonate filter cake at room temperature, evaporator operation for the crystallization of nickel sulfate with its accompanying high energy consumption is eliminated. In addition, 70% of the arsenic is returned with the recovered sulfuric acid back to the tankhouse, ensuring that enough arsenic is present in the electrolyte. Production at the Nickel Carbonation Plant (NCP) commenced in late August 2004.

Nickel Carbonate Plant Optimization

The NCP optimization team was formed in April 2004 with the objective of utilizing the six points of continuous improvement during construction, testing and start-up of the new plant [3, 4]. The team used Quest for Zero tools, identified Key Performance Indicators (KPIs), and established measurements tied to Standard Operating Procedures (SOPs) and Job Safety Analyses (JSAs). There were many incredible things that happened during this period. This team faced challenges, overcame difficulties, and achieved goals. All operators were trained and the MOC was approved during the team activities. There was such tremendous success that the Six Points of Continuous Improvement were achieved, as follows:

Safety: No safety incident; PPE assessments were conducted; the LOTOTO and confined space specific procedures were also reviewed; eyewashes, safety showers, and fire extinguishers were located, checked, and/or installed; 16 SOPs and 16 JSAs were written, reviewed, and logged in the internal website system.

Environmental: No significant spills or releases; eliminated the risk of spilling hazardous waste (black acid); significantly reduced steam use resulting in fewer emissions from Co-Gen; nickel product will have no free acid contained in it making shipping easier; industrial hygiene regulations were reviewed and an MSDS for Nickel Carbonate is being written; an environmental checklist was written and checked.

Quality: KPIs and operational parameters were studied and generated; operational log sheets were generated; APU performance test 100% completed; greater than 90% acid separation by the APU was achieved; dynamic air performance test 100% completed; three operator trainings were conducted; the nickel carbonate filter cake, containing 45% Ni (dry basis) was produced.

Production: Nickel carbonate production—batch sequence was created and used in the operation; we are approaching the designed production rate of treating 10,000 gallons of electrolyte a day; to date, 5 bags of impurity sludge and 22 bags of nickel carbonate, each weighing about 1700 lbs (at about 70% moisture) have been produced.

Cost: Cost reduction and revenue enhancement in the following areas: (1) black acid disposal savings, (2) black acid car rental and shipping savings, (3) sulfuric acid savings, (4) steam savings, and finally (5) difference in nickel metal return of \$1.14 MM/year.

Stakeholder Relations: Employees—safer process; community—cleaner technology; stakeholders—good investment; overall—it is the right thing to do for all our stakeholders!

Conclusion

1. El Paso electrolyte components are typical of traditional tankhouse electrolyte. The El Paso electrolyte shows considerable variability in nickel content that needs to be controlled by daily bleeding a certain volume of electrolyte from the tankhouse.
2. As compared to the current nickel sulfate process in the treatment of tankhouse bleed electrolyte, the new developed process recovers copper, sulfuric acid and purified nickel (as nickel carbonate) that results in eliminating black acid generation and evaporator operation.
3. This innovative environmentally friendly process is first globally developed in the copper refinery. It is a significant sustainable development in the brown field that focuses on saving energy consumption, reduction of carbon dioxide (CO₂), and elimination of hazardous material (black acid) handling.

References

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