

IONEXCHANGE OPERATIONS FOR COPPER AND ZINC RECOVERY AND ARSENIC REMOVAL AT THE DEVNYA WASTE TREATMENT PLANT, BULGARIA

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ABSTRACT. In the past year, design and construction of waste treatment plant for metal recovery and water treatment, located in the industrial area of town of Devnya, Bulgaria was initiated. The first step in the plant flowsheet is regrinding of the waste to a size, which make it amenable to leaching at the temperatures used here (typically up to 180 °C). This is followed by two-stage leaching with recycled raffinate as the leach medium and with oxidant addition. The leach residue is separated from the slurry and washed, while the copper and zinc (and eventually) arsenic rich solution proceeds to ionexchange recovery and removal operations. The copper ionexchange operations with overall annual productivity of 2400 tones copper cathodes consists of two solvent extraction trains, each comprising two extraction stages in series, one wash stage and two stripping stages, followed by sorption facility for final copper recovery and conventional electrowinning in sulfate media. Zinc is recovered from copper-barren raffinate in 3Ex3Wx2S solvent extraction circuit using D2EHPA extractant. The loaded organic is then stripped using spent electrolyte, producing advance electrolyte for recovery of 1200 t/a zinc by electrowinning. The arsenic removal circuit includes two successive steps: 1) two-stage precipitation of arsenic to obtain the insoluble scorodite and 2) final removal of arsenic using specially designed for this purpose ion exchange resin. Operating descriptions and the technological flowsheet of the Plant, as well as experience and performance are provided.

Keywords: ionexchange, solvent extraction, copper, zinc, arsenic

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Relevant Congress topic: Eco-Friendly Technologies for Waste Recycling

INTRODUCTION

The Devnya Waste Treatment Plant (DWTP) uses a hydrometallurgical process route, developed by Iontech Engineering to treat a wide variety of metal-containing wastes. A combination of waste regrinding, two-stage leaching and ionexchange operations, form the core of the technology, which provide a competitive alternative to the traditional pyrometallurgical process routes. Work on the DWTP started in 2010 with laboratory testwork. The development towards commercialization has advanced systematically from laboratory-scale testing through various studies to the design, construction and successful operation of a demonstration plant at the Iontech's Tzar Asen Copper plant. In 2012 starts the execution of hydrometallurgical DWTP, which is designed to produce 2400 tpa copper as LME grade cathodes and 1200 tpa zinc as a LME (SHG) zinc cathodes (Tsekov, V. at all, 2003).

WASTES, PROVIDED FOR TREATMENT

According to the Regulation on the requirements for treatment and transportation of industrial and hazardous waste (adopted with Decree of the Council of Ministers No 53 from 1999; State Gazette No 29/1999) (MOEW, 2009), wastes at DWTP will be treated via operations, which lead to resource recovery, recycling or reuse, namely R3 - Recycling/reclamation of metals and metal compounds

The type of wastes and the valuable metal content are given in Table 1.

Table 1. Waste name, code and metal content

№	Waste name and code	Metal content % (g/t)				
		Cu	Zn	Pb	(Au)	(Ag)
1	Electrofilter dusts 100603*	25%	9%	31%	40	140
2	Lead dusts, 100603*	3%	8%	45%	1	120
3	Baghouse filter dusts 101009*	5%	55%	0%	0	0
4	Filter cakes 110205*	45%	5%	5%	0	300
5	Galvanic sludge 11 0109*	15%	45%	0%	0	0
6	Metal casting slag, 1010 03	27%	40%	0%	0	0
7	Spent batteries 16 0601*			55%		
8	Spent catalyts 16 08 02*	-	-	-	-	-

THE GENERAL FLOWSHEET FOR THE DWTP PROCESS

The general flow sheet for the DWTP process is shown in Figure 1. The wastes are trucked to the DWTP, where the wastes is reground using one super pressure trapezoid mill. The mill product is subjected to the first leach stage (atmospheric leach circuit), where the slurry reacts with sulfuric acid to produce copper and zinc sulphates in solution for downstream recovery.

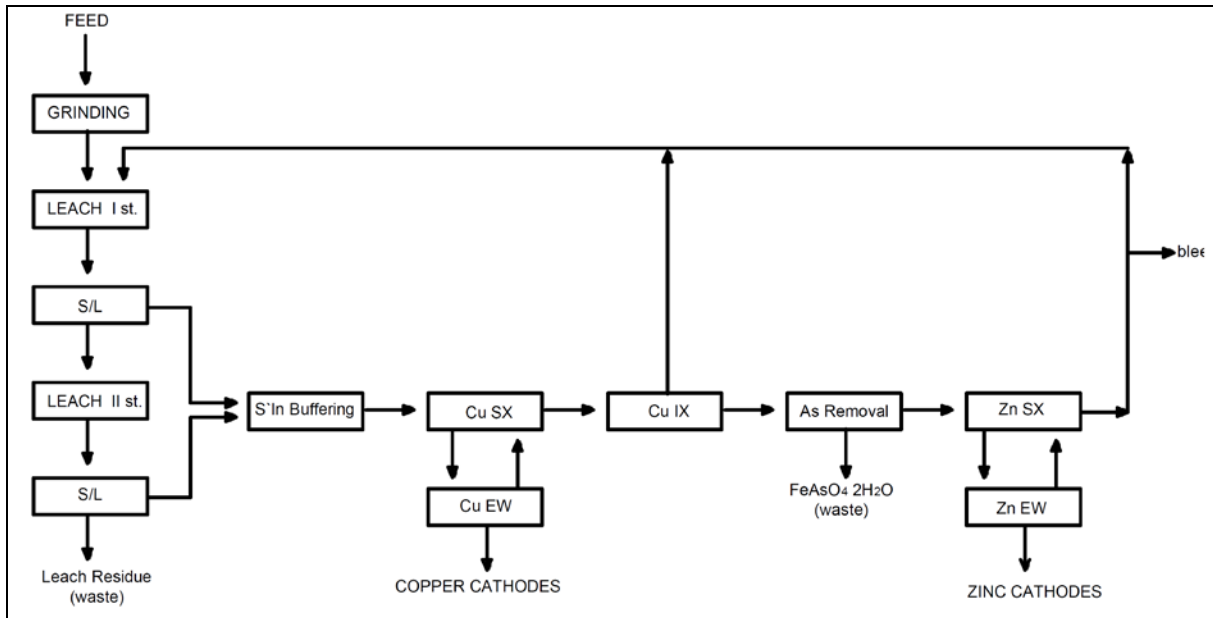


Figure 1. The general flow sheet for the DWTP process

The atmospheric leach circuit comprises nine 10 cubic meters agitated tanks with air sparging. Leaching is carried out at ambient temperature and at a density of 20% solids. The acid level in the atmospheric leach discharge is controlled by the net acid consumption and through controlled acid addition to the circuit, on an as-needs basis. Discharge acid levels in the range 5–10 g/L are targeted. The leach slurry goes to a solid-liquid separation section, from where the solid residue is reported to a second leach stage and solution to the buffering solution tank. The leach residue from previous leach stage is fed to two 5 cubic meters parallel autoclaves where the slurry reacts with sulfuric acid at high pressure and temperatures and residual copper and zinc are almost completely leached for a leach residence time of 4 hrs. Next the leach slurry is filtered in filter press, solution, rich in copper and zinc are sent to buffering solution tank and the cake is final waste.

Copper and zinc containing solution is contacted with an organic reagent in the copper SX circuit that selectively extracts copper from the solution. Copper is stripped from the organic using spent electrolyte from the copper EW circuit. The rich electrolyte is treated to remove trace organic before being pumped to the Cu EW circuit. The copper SX raffinate is advanced to the polishing stage-copper Ion Exchange circuit - where the rest of the copper is recovered and recirculated back to the first leach stage. The copper-rich electrolyte is sent to the Cu EW circuit to produce copper as LME grade copper cathode. Spent electrolyte is recirculated back to copper SX for enrichment via stripping of the copper-loaded organic phase. Arsenic in the copper IX circuit filtrate is removed, in a two-stage removal circuit and arsenic free, zinc-containing solution is advanced to Zinc SX circuit. Here the zinc solution is contacted with an organic reagent that selectively extracts zinc from solution. Zinc is stripped from the loaded organic phase with spent zinc electrolyte recirculated from zinc electrowinning circuit (Zn EW). The rich electrolyte is treated to remove trace organic before reporting to the Zn EW cell house. The Zn SX raffinate stream is transferred back to the first leach

stage. The Zn EW process is designed to produce SHG zinc cathode. Recovered spent electrolyte from Zn EW is then recirculated to zinc SX for stripping (Angelov, T. et al., 2011).

DESCRIPTION OF DEVNYA WASTE TREATMENT PLANT (DWTP)

Description Of The DWTP Solvent Extraction (SX) Circuits

Copper SX circuit

Copper is selectively transferred from the relative low grade copper solution into a high-purity electrolyte stream using a copper selective extractant. The extractant employed is an oxime based copper-selective chelating reagent that is dissolved in a high flashpoint hydrocarbon diluent to make up the organic phase.

The copper solvent extraction circuit consists of three main process steps:

- Extraction-copper containing solution is contacted with the stripped organic phase in two extraction stages to transfer copper from the aqueous to the organic phase
- Wash-the loaded organic is washing with acidic demineralized water (5-10 g/l sulfuric acid) in one wash stage to remove co-extracted iron and aqueous-entrained chloride and manganese. Although extractant high selectivity for copper over most other cationic species under extraction conditions, a small quantity of iron is co-extracted. The wash stage minimizes entrainment of aqueous in the loaded organic phase, that otherwise will result in the undesirable build-up chloride and manganese in the electrolyte.
- Stripping-the washed organic phase is contacted with spent electrolyte from electrowinning in two stages, utilizing the acid generated during the copper deposition process. Copper is transferred from the organic into an aqueous phase.

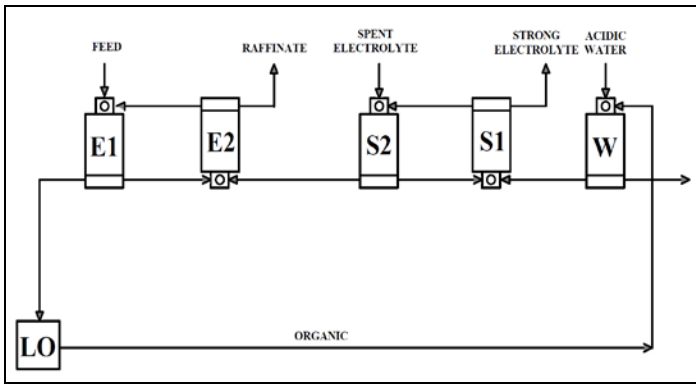


Figure 2. Copper SX Circuit

Zinc SX circuit

Zinc is recovered from the zinc containing solution following the arsenic removal process, using a solvent extraction circuit. The extractant employed is the di-2-ethyl hexyl phosphoric acid (D2EHPA,) diluted in a high flashpoint hydrocarbon diluent. This provides selective extraction for zinc by controlling the pH in the extraction stages.

The zinc solvent extraction circuit consists of three main process steps:

- Extraction-purified feed solution is contacted with stripped organic phase and zinc is transferred from the aqueous to the organic phase in three stages. The pH is controlled by the addition of ammonium hydroxide.
- Wash-the washing process takes place in three stages. The first two use demineralized water to wash out physically entrained impurity species; spent electrolyte is employed as a wash liquor in the third wash stage to 'crowd off' co-extracted impurities from the loaded organic.
- Stripping-the loaded organic is contacted with acidified zinc strip liquor and the zinc is transferred from the organic to the aqueous phase in two stages

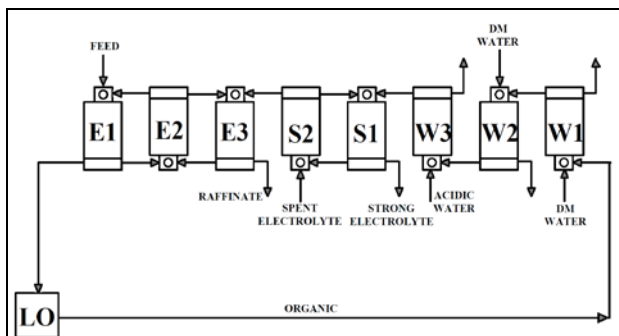


Figure3.Zinc SX circuit

Configuration of the DWTP Solvent Extraction (SX) circuits

The Table 1 below shows a comparison between the two SX circuits for DWTP. Parameters compared are type of extractant and diluent, temperature, number of trains, configuration and existence of pH control, methods for organic and crud recovery and treatment.

Table 2.Comparison of the DWTP SX circuits

	Copper SX	Zinc SX
Extractant	LIX 84-I	D2EHPA
Extractant family	Hydroxy Oxime	Organo-phosphorus
Diluent type	Hydrotreated Distillate, Light C9-C16 Paraffinic and Aromatic Hydrocarbon (high flash point)	Hydrotreated Distillate, Light C9-C16 Paraffinic and Aromatic Hydrocarbon (high flash point)
Temperature	25-30°C	40-45°C
Nr of trains	2	1
Configuration	2E x 1W x 2S	3E x 3W x 2S
Flow pattern	Conventional Flow	Conventional Flow
Loaded Organic tank	Yes	Yes
pH control in extraction stages	No	Yes(ammonium hydroxide)
Organic recovery	Flotation Column /Dual media Filter	Flotation Column /Dual media Filter
Crud treatment method	mixing with acidic water	mixing with acidic water
Organic treatment method	Clay mixing and separation of phases by Filter Press	Treatment with 6M HCl (optional)

Equipment, used in the DWTP Solvent Extraction (SX) circuits

The DWTP Solvent Extraction (SX) circuits design is based on the use of the countercurrent mixer-settler concept. Each mixer-settler consists of a one-stage mixer and a settler. The mixing system provides high stage efficiency ensuring sufficient retention time in the mixers (3 minutes for the two SX circuits). The mixing tank is fitted with a pump-mix type impeller, which provides the head for the inter-stage pumping of solutions as well as mixing of the two phases. It incorporates a false bottom into which the organic, aqueous and recycle streams are introduced. The dispersion overflows into a settler where sufficient area is provided for disengagement of the aqueous and organic phases (settler specific flow rate is about 4 m³/h/m² for both circuits). A weir arrangement at the discharge end of the settler allows for separate discharge of the organic and aqueous phases. The aqueous/organic interface level in the settler is set during commissioning by manual adjustment of the physical height of the aqueous overflow weir. The design allows all the mixer-settlers to run with organic or aqueous continuity by adjusting the internal recycles to the mixer from the settler. (Jergensen,1999)

Description Of The Copper Ion Exchange (IX) Circuit

The Copper Ion Exchange (IX) circuit is designed in order to recover remaining copper from Copper SX circuit. It consists of 2 columns in series, each with single chamber

with top and bottom nozzle plates that is filled with copper selective resin(Brings). Feed solution-copper SX raffinate, is pumped through the top of the first column filled with ion exchange resin, out the bottom and into the bottom of the second column. From the top of the second column the barren solution, called filtrate is sent to arsenic removal circuit.

When the resin in the first column is fully loaded with copper, it is disconnect from the line, while the second is maintained active to process more solutions, but in downflow mode.

Regeneration of the first column with a sulfuric acid solution (160-200 g/l H₂SO₄) produces a regenerate, which is stored in buffer tank. Next the buffered regenerate is pumped back to first leach stage.

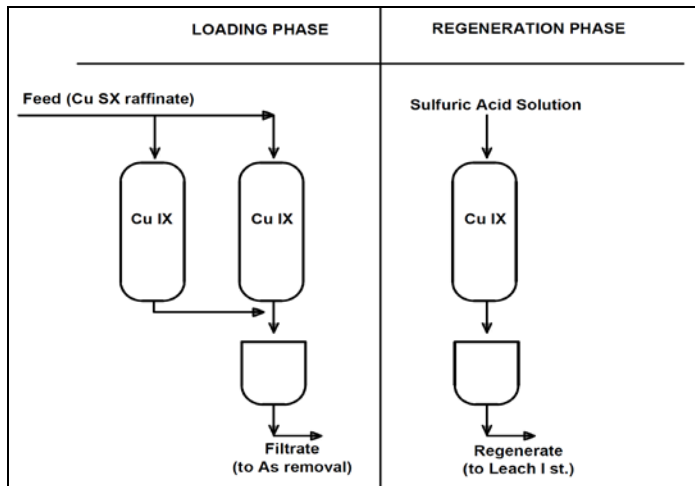


Figure 4.Copper IX circuit

Description Of The Arsenic Removal Circuit

Arsenic removal takes place in two successive stages: 1) two-stage precipitation of arsenic to obtain the insoluble scorodite and 2) final removal of arsenic using ion exchange resin. Filtrate after ion exchange removal of copper is sent to a two-stage scorodite precipitation circuit. In this circuit, ferric sulfate is added at a stoichiometric ratio to arsenic together with recycled scorodite/gypsum seed. A retention time of four hours is necessary for the removal of 95% of arsenic in the form of crystalline scorodite by stepwise neutralization with slaked lime at 90°C. The resulting slurry is filtered by a filterpress. Part of the filter cake is recycled to the first scorodite precipitation tank, where the scorodite-seed concentration must be maintained at a minimum of 50 g/l. The filtrate is pumped to the second precipitation stage, where the rest of the arsenic is precipitated at pH 3 as amorphous arsenate-hydroxide compounds that, after filtering are recycled back to the scorodite precipitation stage and solution is subjected to the polishing stage, which is the key unit of arsenic removal circuit. The polishing stage comprising two ionexchange column, filled with specially designed for this purpose resin. In comparison to classical strongly basic anion exchange resins, this resin selectively adsorbs arsenic, i.e., other ions such as chloride, sulphate or nitrate are not bound to the resin and therefore, do not significantly influence the uptake of arsenic on the adsorber. Another positive effect is that arsenic, once it is adsorbed, cannot be desorbed by these competing ions Therefore, the total capacity of

this resin is significantly higher compared to a conventional anion exchange resin. (Neumann,2009)

The feed solution (from precipitation circuit) is pumped through the columns, passing the resin beds. The resin saturation carried out in the first column, while the second is used to capture missed arsenic. The filtrate, which is completely free of arsenic, is advanced to the Zn SX circuit. After the appearance of “breakthrough” in the first column it is subjected to regeneration and adsorption continues only into the second column. For regeneration an aqueous solution of 2 % NaOH and 3% NaCl is applied at a flow rate of 3 BV/h. Then, the resin is rinsed with 8~10 BV of demineralized water. The combined regenerate and the rinse water is acidified to pH 2. Then iron (III) sulfate is added followed by a neutralization to precipitate FeAsO₄. The sludge is filtered and recycled to the precipitation circuit.

In this manner, all arsenic entering the arsenic removal circuit is effectively immobilized and removed as crystalline scorodite.

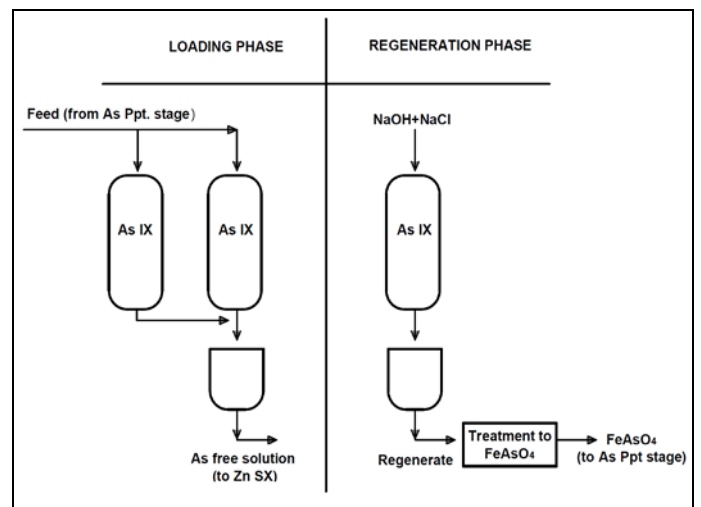


Figure 5. Arsenic removal circuit

PROJECTED DEVNYA WASTE TREATMENT PLANT (DWTP) PERFORMANCE

Table 3.Projected DWTP performance

	Copper	Zinc	Arsenic
Flowrate,m ³ /h	2 x 18.0	20.0	18.0
Concentration in the feed, g/l	10.0-15.0 (for SX) 0.5-0.75 (for IX)	10.0	2.0-10.0
Effluent concentration, g/l	0.5-0.75 (after SX) 0.04-0.06 (after IX)	1.0	0.0002
Recovery,%	95 for SX 92 for IX	90	99
Product t/y	2400	1200	-
Product Quality	LME (High Purity Grade) Copper Cathode	LME (Special High Grade) Zinc Cathode	-

CONCLUSION

The mining and metallurgical industries produce many types of waste streams. Increasing costs and stricter regulations require more effective methods for treatment of these wastes. One of the most important tasks is the removal or recovery heavy metals. The effective recovery of these metals is possible only if the separation process is selective enough. Ion Exchange operations, namely Solvent Extraction and Adsorption, can be used in very effective manner for reducing the amount of metal in the wastes as well as for purification of process liquids for re-use and for the treatment of final wastes. The net result of the use of Ion Exchange operations is that valuable metals can be produced from sources that in the past would have gone untouched. Further, the process is capable of removing metals from waste materials, which otherwise are considered a severe contaminant to the environment.

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