PILOT TEST OF EMEW® TECHNOLOGY APPLICATION TO COPPER ELECTROREFINERY BLEED STREAMS WITH HIGH ARSENIC CONTENT

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ABSTRACT

The results of a three month evaluation of the application of EMEW® technology at the KGHM Głogów II Smelter tank house bleed stream are presented. The current, conventional electrolyte deopperization process has some limitations, including: only a fraction of its production is commercial grade cathode copper, significant operating costs, low current efficiency, low current densities resulting in low copper depletion rate, and arsine gas and sulphuric acid emission. The EMEW® cell technology developed by Electrometals Technologies Ltd. can overcome many of these limitations. Tests were performed on a pilot EMEW® installation comprising 30 cells at ambient temperature on electrolyte bleed, using current densities between 100 and 600 A/m^2 , with copper concentrations between 45 and <1g/dm^3. Results showed that a high grade copper can be obtained to the level of 7 g/dm^3 of copper concentration in electrolyte. The use of EMEW® technology allows the direct and efficient recovery of over 85% of the copper contained in the bleed electrolyte. Glue & thiourea addition were tested in order to improve the parameters of the copper depletion process. The behavior of Arsenic and Bismuth was observed and a means for their elimination from the system proposed. On-line copper concentration monitoring is proposed to improve control and performance.

INTRODUCTION

The depletion process of bleed electrolyte stream carried out at Głogów Smelter II Tank House, which is essential for maintaining the highest quality of the cathode copper product, is performed using conventional technology. It is burdened with some of faults and disadvantages, for example:

- recovery of the fraction of product as a commercial grade cathodes. Cascade copper and copper-arsenic gangue along with significant quantity of contaminants are recycled to the copper pyrometallurgical process also requiring the production of copper starting sheets
- significant operational costs connected with high unit energy consumption
- low current process efficiency, especially in case of deep copper depletion;
- low current densities – consequently low copper depletion rate
- Arsenic gas and sulfuric acid moist emission and resulting Personal Work Protection Hazard and Environment contamination.
- High labour charges associated with preparing of the starting sheets and handling sludges from the process

The newly available EMEW® technology equipped with insoluble, Dimensionally Stable Anodes (DSA®) made of titanium with iridium oxide coating, carried out in cascade tanks presents an alternative to conventional technology of bleed electrolyte stream treatment. The technology developed by Electrometals Technologies Ltd – Queensland, Australia characterizes with new construction solution of the copper depletion electrolysers. The new EMEW® technology of the electrolytic copper depletion ensures:

- Operation at current densities that are at least 100% greater than the conventional copper technology
- Enhancement of quality of produced copper. The purity of copper is saleable commercial grade
- Reduction of the operational costs
- Improvement of work safety for the operators

Owing to tri-lateral agreement of KGHM Polska Miedz S.A. and De Nora (Italy) and Electrometals Technologies Ltd (Australia) a pilot installation of EMEW® technology was installed at KGHM's Glogow Smelter II Tank House.

It comprises of a 30 cell frame. The assembly of the installation was carried out under supervision of the De Nora specialists. The tests performed aimed to verifying of the proposed technology in HM Głogów II operational conditions. They took place in period May-July 2005 in accordance with developed and agreed research program and data registration system.

DESCRIPTION OF EMEW® COPPPER PILOT PLANT EQUIPMENT

The EMEW® pilot installation comprises the set of 30-cells, arranged in two rows of 15 tube-cells each (Fig1). Its module construction was built on support frame with dimensions 6m x3m. The installation height is ca. 2,1m. The cells are tubes in shape with diameter 150mm, made of acid-proof stainless steel with caps and solution inlets at the bottom and outlets at the top made of ABS plastic. The electrolyte is inserted concentrically, which causes its spiral flow from the bottom to the top of the cell.

The cathode starter sheet is made of acid-proof stainless steel 316L type, with thickness 0,6mm, and dimensions 2100 x 485mm folded in a roll shape. It is inserted into the cell pipe and tightly contacts to its inner surface. The overlap of the cathode sheet is ca 10mm and is overlapped in the direction of electrolyte flow. The cathode surface is 0,5m^2. The current is applied to the stainless steel cell body.

The insoluble anode (DSA®) made of titanium tube 50mm in diameter, coated with iridium oxide, is employed in the EMEW® cell. The anode is placed coaxially and fixed to bottom cap of the cell. The active anode surface is about 0,18m^2. The distance between cathode and anode surfaces is about 50mm. The cells are connected in series in two current circuits, 2x15 cells: circuit I (1-15) and circuit II (16-30). Each circuit is powered from separate direct current rectifier. The electrolyte flows through all cells in parallel, it comes from collectors which are fed from reservoir tank with capacity 60m^3. The electrolyte flow is forced by the centrifugal pump situated under the tank which has capacity of 90m^3/h, lifting height 15m, electrical power 11kW, rotations 1450/min and rotor diameter 240mm. Flow rate to each cell is approximately 5 m^3/h.

SCOPE OF EMEW® PILOT CELL TESTS

- Demonstration of EMEW® technology compared to conventional copper depletion technology
- Optimization of the important process variables to produce commercial grade copper product

TEST METHODOLOGY

The electrolyte copper depletion tests on the pilot EMEW® installation at Głogów II Smelter were carried out in the period of May - July 2005.Twelve copper depletion cycles were performed. The electrolyte to be tested was taken from electrolyte stored in Decopperization Department tanks. In the so called periodic batch depletion tests, the copper content in electrolyte was lowered to the required concentration level. After reaching this level the test were carried in the continuous mode, which constituted the main part of the tests. The so called continuous tests were carried while maintaining the constant copper content in electrolyte flow at the levels of Cu^{2+} around 20g/ dm^3 or around 5 g/ dm^3.

In total 6 continuous tests were carried out, two of them at 20 g/dm^3 Cu^{+2} , and the remaining four tests were carried in the constant copper level of Cu^{+2} 5 g/dm^3.

This paper focuses mainly on the tests carried out in the continuous mode. In the continuous tests the constant copper content of the circulating electrolyte was maintained by the permanent inflow of fresh electrolyte from the reservoir tanks coupled with constant outflow of its equal quantities from the circuit.

About every 8 hours the electrolyte samples were taken and analyzed for Cu^{2+} and H_2SO_4 contents, and from time to time for the arsenic content. After the end of the test, the electric current was switched off, circulation was suspended, the electrolyte transferred from the cells into the circulation tank and the copper product deposited inside was washed out by filling the cells with water. The volume of water washing one cathode portion deposited in 30 cells was around 1m^3, the washing time about 25-30 min. Due to the small water connection this method is slow and it is recommended that the copper product be washed in a conventional cathode wash bath.

The copper deposit after manual detaching from the stainless steel cathodes, was transferred to a storage facility, then weighed and labeled.

Additional tests (tests IV and X in Tables I and II) aimed to explore low inlet Cu concentrations (between 5 and <1 g/dm3) were performed, even though it was presumed that less solid Cu deposits would be produced (even in the form of copper-arsenic sponge), which would be more difficult to remove from the cells using methods described above. Copper-arsenic sponge/powder is more easily handled in the fully-automated EMEW® powder cells which were not in the scope of this test program. Therefore, before commencement of the depletion tests below 5g/ dm^3, the process of maintaining constant copper Cu^{2+} concentration level around 5g/dm3 in electrolyte was carried out, on the principles described earlier. Only after obtaining solid copper deposit on the cathodes, the fresh electrolyte inflow was stopped and the electrolyte depletion process into the final stages performed. The analytical samples were taken by drilling 4-5 holes in one of the cathodes produced during the test, along its length in roughly equal intervals.

KEY TECHNOLOGICAL INDICATORS OF EMEW$_{®}$ COPPER DEPLETION

The key technological indicators of the copper depletion process obtained in the pilot tests performed on EMEW$_{®}$ technology are presented in the table below:

Test	Type of test	Time of test	Current circuit I		Current circuit II		Cu^{2+} concentration [g/dm^3]		Mass of product [kg]		Current efficiency		Direct Current power consumption [kWh/t Cu]	
			Current [A]	Voltage [V]	Current [A]	Voltage [V]	start	finish	Circuit I	Circuit II	Circuit I	Circuit II	Circuit I	Circuit II
I	Periodical	72,0	232,0	39,87	189,0	36,56	46	20	280	222	94,2	91,7	2381,1	2242,99
II	Continuous	68,0	232,0	40,35	189,0	37,17	20	20	260	210	92,6	91,8	2451,14	2277,93
III	Periodical	93,0	121,0	31,33	-	-	22	7	180	-	89,8	-	1961,14	
IV	Periodical	141,0	-	-	92,0	28,56	22	0	-	216		93,6		1751,17
V	Periodical	71,0	298,0	42,14	277,0	41,20	48	19,2	350	322	93,3	92,4	2540,99	2508,51
VI	Continuous	72,0	298,0	41,78	275,0	40,76	19,2	21,49	352	324	92,6	92,4	2538,33	2481,72
VII	Periodical	91,0	175,0	36,09	150,0	34,87	21,49	5	354	222	89,5	91,3	2268,58	2148,68
VIII	Continuous	167,0	125,0	34,12	100,0	32,58	4,06	5,91	330	266	88,7	89,4	2164,09	2050,24
IX	Continuous	259,0	75,0	29,63	50,0	27,32	5	5	292	184	84,5	79,9	1972,72	1923,64
X	Continuous	208,0	75,0	29,74	50,0	27,44	5	5						
	Periodical	90,0	75,0	30,53	50,0	28,01	5	0	332	174	83,5	65,6	2019,83	1860,39
XI	Continuous	143,0	138,0	29,22	118,0	31,67	5	5	268	242	88,1	80,6	1865,93	2210,57
XII	Continuous	170,0	118,0	27,93	100,0	30,52	5	5	274	254	88,6	84,0	1773,49	2044,07

Circuit I cells: 1-15
Circuit II cells: 16-30

Table 1 - Basic indicators of the copper depletion obtained in the EMEW® technology

The technological indicators obtained in the continuous copper depletion tests, the ones which maintained Cu^{2+} concentration levels around 20 g/dm^3 or 5 g.dm^3, as well as the additional tests aimed at achieving "complete" copper depletion to Cu^{2+} content <1 g/dm^3 are presented in the table below. The results are presented in order of increasing current density, in each of copper concentration level in electrolyte.

# Test	Cell number	# electric circuit	Current density [A/m2]	Avrg voltage [V]	Cathode mass [kg]	Current efficiency [%]	Power consumption [kWh/h]
Cu^{2+} concentration – ca. 20g/dm^3							
II	16-30	II	378	37,17	210	91,8	2277,93
	1-15	I	464	40,35	262	91,6	2451,14
VI	16-30	II	550	40,76	324	92,4	2481,72
	1-15	I	594	41,78	352	92,6	2538,33
Cu^{2+} concentration – ca. 5g/dm^3							
IX	16-30	II	200	27,32	184	79,9	1923,64
VIII	16-30	II	200	32,58	266	89,4	2050,24
XII	16-30	II	200	30,52	254	84,0	2044,07
	1-15	I	236	27,93	274	88,6	1773,49
XI	16-30	II	236	31,67	242	80,6	2210,57
VIII	1-15	I	250	31,12	330	88,7	2164,09
XI		I	276	29,22	268	88,1	2210,57
Periodical test – total depletion from Cu^{2+} concentration – 5g/dm^3 to 0,X g/dm^3							
X	16-30	II	100	27,61	292	65,6	1860,39
	1-15	I	150	29,97	332	83,5	2019,83
IV[1]	16-30	II	184	28,56	216	93,6	1715,17

1) copper depletion from 22 g/dm^3----0 g/dm^3

Table 2 - Basic indicators of the copper depletion obtained in the EMEW® technology

TEST RESULTS SUMMARY

The electrolytic copper obtained in the overwhelming majority of copper depletion tests performed on the pilot EMEW® installation, from both the continuous and the periodic batch depletion tests, had the degree of purity qualifying it for commercial grade Cu CATH 1 or Cu CATH 2.

In the continuous copper depletion tests at Cu^{2+} levels around 20 g/dm^3, at current densities 378 A/m^2 and 464 A/m^2 the cathodes produced had the purity of Cu grade CATH 1. At higher electric current densities of 550 A/m^2 and 594 A/m^2 the cathodes produced had the purity of Cu grade CATH 2.

It could be assumed that the maximum current density in continuous mode of copper depletion performed on EMEW® installation which allows the production of electrolytic copper grade Cu CATH1, would be around 500 A/m^2.

In the continuous tests in which the copper concentration level in circulating electrolyte was maintained around 5 g/dm^3 the cathodes of grade Cu CATH 2 were obtained from the entire tested range of current densities from 100 to 276 A/m^2. In the prevailing number of cases, the reason for qualifying the cathodes to the lower grade was higher sulphur and arsenic contents.

On the grounds of the test results analysis it could be assumed that the recommended current density for continuous copper depletion at the copper concentration level in electrolyte around 5 g/dm^3 should not exceed ca.250 A/m^2.

In the "complete" copper depletion tests with copper concentration Cu^{2+} ca. 5g/dm^3 to <1,0 g/dm^3 carried out at low current densities 100 and 150 A/m^2 the quality of copper produced was of Cu CATH 2 grade.

During the tests in which the current density was increased to 168 A/m^2 the cathodes produced had extremely high contamination level, well outside the limits of commercial copper grades. In the tests of "complete" copper depletion the sponge copper was found on the cathode surfaces which was probably partially removed by the electrolyte flow, and dropped during cathode harvesting.

In the continuous copper depletion process, performed at copper concentration of ca. 20 g/dm^3, for the entire range of current densities used i.e. 378 – 594 A/m^2 high or close to it current efficiencies of 91.6 % - 92.6 % were achieved. With the increase of current density the rise in the cell voltage and resulting increase in unit energy consumption were noticed. In the tested electric current density range the increase of energy consumption was ca 305,4 kWh/t Cu i.e. about 13,4 %. As expected, operation at high current density required higher cell voltage. It is expected that the cell voltage will be reduced when running at normal liberator circuit electrolyte temperatures of 50-65^{o}C.

During continuous copper depletion tests with copper concentration level in electrolyte of ca 5 g/dm^3 and current densities within the range of 200 – 276 A/m^2, the current efficiency indicator was at the level of 79,9 – 89,4 % (avg. 85,6 %). In the tests performed the electric energy consumption indicator of direct current ranged from 1773,5 kWh/t Cu to 2210,6 kWh/t Cu, with the average of 2053,8 kWh/t Cu. The tests didn't demonstrate any distinct correlation between current efficiency, cell voltage, and energy consumption based on current density within the tested range of this parameter. It should be noted that the energy consumption and voltage on the cell module is lower in case of copper depletion carried out at the levels of Cu^{2+} ca 5 g/dm^3 in electrolyte, than carried out at the level of ca.20 g/dm^3. It probably results from the difference cell voltage and increased conductivity due to sulphuric acid concentration.

The "complete" copper depletion tests which reached the levels of Cu^{2+} <1 g/dm^3 of copper concentration performed within the range 100 – 184 A/m^2 current densities, demonstrated significant differences in current efficiency (65,6 – 93,6%), as well as voltage values at cells and the consumption of direct current.

During the tests a number of observations were made which could be significant for the industrial scale exploitation of the EMEW® technology. Scale up from Pilot Plant to commercial operation is expected to significantly improve efficiency of materials handling and operating procedures.

- The duration of cathode washing is rather time-consuming. The washing of the cathodes of total weight around 500 – 700 kg took ca 30 min. Moreover, the cathode washing in the cells is inefficient, which is proven by the increased sulfur content in the copper produced. It is also the cause of large water consumption – the washing of one lot of copper produced during one test requires ca 1 m^3 of water. A conventional tank wash system is recommended.
- The time required for shim exchange at the end of the cathode cycle is long-lasting and it takes an average 2,7 hours for single 30 cell module. In the pilot plant setting with the large overhead crane the shim exchange requires three people which is time consuming. It is assumed that in industrial version the shim exchange will be satisfactorily improved and mechanically operated. As a result of these concerns, automated harvesting is being actively developed by Electrometals. Standard harvest procedures and possibly automated harvesting is recommended. Bench mark harvest rates are approximately 2.2 man-hours per metric tonne of cathode (based on 30kg cathode weight).
- Though there was some consumption of parts including copper starter sheets and o-ring seals these were mainly a result of testing under non standard conditions as was necessary during the test program and consumption is expected to be significantly lower in a commercial cell operated under steady conditions.

In the electrolyte depletion process performed continuously on EMEW® pilot installation at Cu^{2+} concentrations levels of ca 20 g/dm^3 and ca 5 g/dm^3 practically all arsenic load remains in the solution and it is transferred to the second stage of copper depletion (the level of Cu^{2+} - ca 5 g/dm^3). Having confirmed the lack of AsH_3 emission, the drop of the As concentration in the solution due to its presence in electrolytic copper produced is ca $0,3 \cdot 10^{-3}$ g/dm^3, so the change in its concentration is very hard to detect by the analytical methods used. The arsenic gas measurements on pilot installation made on ventilation chimney outlet did not detect any arsine gas presence.

CONCLUSIONS.

1. The tests performed demonstrated that application of the EMEW® enables the recovery ca 89,5% copper contained in the depleted electrolyte, as a cathode copper form with commercial purity according to the Standards.
2. Electrolyte copper depletion process using EMEW® technology enables application of high current densities. It was demonstrated that to guarantee the high quality and purity of cathode it is reasonable to use the following current densities: 500 A/m^2 – I Stage of continuous depletion, at copper concentration in electrolyte ca. 20 g/dm^3 and 250 A/m^2 – II stage of continuous depletion, at maintaining Cu concentration – ca 5 g/dm^3. For these conditions the high current efficiency indicators of 92% and 88,6% are obtained.
3. There was no arsine gas emission for continuously operated copper electrolyte depletion, while maintaining copper concentration in electrolyte on the level ca 20 g/dm^3 – I stage and 5 g/dm^3 – II stage.
4. The observations and analyse of the technological process have shown that:

- In situ Cathode washing process during exchanging of the cell module cathode inserts (30 cells) is long-term (avrg. 30'), low efficient (high S content in product) and significantly water consuming – ca 1m^3 water 600 – 700 kg cathodes washing. It is recommended that conventional cathode washing by dipping in water bath be used.
- The changing of the cathode inserts was labour and time consuming. For 30 cells work preparation requires ca 8 man-hours (3 person x avrg. 2,7 h). Improved efficieny of commercial operation should reduce this time by 70%. In addition, as a result of these concerns automated harvesting is being actively developed by Electrometals.
- If solids are not removed from the electrolyte dendrite formation can cause short-circuits which require cell opening for removal.
- Copper produced at continuous concentration of ca 5 g/dm^3 was brittle. Recommend batch depletion rather than continuous operation at 5 g/dm^3 for coherent copper.

The positive results concerning of the copper cathode quality produced by the EMEW® pilot installation are sufficient motivation for tests continuing in KGHM conditions.