15th International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2011, Prague, Czech Republic, 12-18 September 2011

CONCEPTUAL SOLUTION OF FLEXIBLE PLANT FOR COPPER (II) CHLORIDE PRODUCTION

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ABSTRACT
The experimental investigation, was determined the optimum technology for copper(II)chloride production by dissolution of Cu with nitro-hydrochloric acid. As copper recovery in the process could be of high quality, a proposal was given for this salt by re-crystallization of the 2nd crystals $CuCl_2 \cdot 2H_2O$ and was made the total use of copper to the 99.80wt.%.. The material balance calculation of raw material and power resources was carried out, including a balance of waste water and waste gas, and conceptual solution for flexible technology line was carried out for copper salts production.
Keywords: copper (II) chloride, copper, nitro-hydrochloric acid, re-crystallization

1. INTRODUCTION
By the request of the Copper Mining and Smelting Complex Bor (RTB Bor), the preliminary project of flexible plant for production of many inorganic metals salts was determined. The experiments of this technology were investigated and by preliminary project plant, a technical line for production copper (II) chloride, $CuCl_2 \cdot 2H_2O$, in request quantity of 3000 kg /year was adopted. Based on the experimental investigations, the optimum technology was determined for production of this salt by copper dissolution with nitro-hydrochloric acid [1,2,3,].Two technological processes for production copper (II) chloride were given generally in new literature. Both of them define dissolution of cathode copper, like raw material. The new data was verified in laboratories researches. These investigations was carried out that the most economic process for winning Cu (II) chloride is copper dissolution in nitro-hydrochloric acid. This process includes the calculation of raw materials and a balance of waste water and waste gas.
The calculation of flexible production capacity was determined, and the technical request and proposals for its project was given. It is necessary to note that proposal of technical process entirely corresponding to the request for production of all listed copper salts: $CuSO_4 \cdot 5H_2O$, $CuCl_2 \cdot 2H_2O$, $CuCO_3 \cdot Cu(OH)_2$, $Cu(NO)_3 \cdot 3H_2O$.

2. EXPERIMENTAL PART
The experiments were carried out in the Mining and Metallurgy Institute (IMMI) laboratories by the cathode copper samples of 50g, and chemicals of pure quality (36% HCl, 65% HNO_3 and ethyl alcohol). Distilled water and energy power are material and working fluids. Copper (II) chloride, $CuCl_2 \cdot 2H_2O$ is bivalent copper salt. It crystallizes by two water molecules in a form of non hygroscopic green crystal.$CuCl_2$ salt dissolves in water, (100 g the distilled water dissolve 110,4g $CuCl_2 \cdot 2H_2O$ at 0^oC; 100 g the distilled water dissolve 194g wt this metal salts). Copper (II) chloride loses crystal water at 100^oC. $CuCl_2 \cdot 2H_2O$ used in the mineral oil industry, metallurgy and organic

syntheses, insecticides production, wood impregnation, pyrotechnic and occasionally in catalysis. $CuCl_2 \cdot 2H_2O$ could be produced by different methods [1,5,6,7]:

1. By the use of hydrochloric acid on copper carbonate:
$$CuCO_3 + 2HCl = CuCl_2 + H_2O + CO_2$$
2. By copper dissolution in hydrochloric acid with oxidants, the air and hydrogen peroxide:
$$Cu + 2HCl + \tfrac{1}{2} O_2 = CuCl_2 + H_2O$$
3. By copper dissolution in nitro-hydrochloric acid:
$$3Cu + 6HCl + 2HNO_3 = 3CuCl_2 + 2NO + 4H_2O$$

Based on the fact that the process of copper dissolution in hydrochloric acid needs long time, the method of dissolution in nitro-hydrochloric acid was accepted and presented on Figure 1.
This process is faster and the most economical and those products save the chemical and energy power.

3. RESULTS AND DISCUSSION

Based on the request, the yearly capacity of 3000 kg the first crystals, the calculation of productive $CuCl_2 \cdot 2H_2O$ line was determined. The basic data of technical process capacity calculation are: productive capacity $CuCl_2 \cdot 2H_2O$ is 3000 kg/year; productive capacity of charge is 34 kg; request quantity Cu/unit product is 0.41kg; crystallization percent $CuCl_2 \cdot 2H_2O$ is wt 90 %; consumption of 36%HCl per unit product is 1.15 l; the total production one charge time is 24 h; the working days per year are 88; charge number per year is 88.Production lines include: one closed type digester for the reactor setting; one vacuum digester for evaporation setting; one digester for crystallization vessels; two closed reactor with mixer – each of them are the total volume of 50 l; two vacuum evaporation volume of 50 l; vacuum filter with hood; three crystallization vessels – each of them are total volume of 20 l; two centrifugal pumps for the solution transport; the centrifuge; the vacuum dryer; the precision technical balance; one closed reservoir for the first (I) mother liquor; one reservoir for dry crystals; the laboratory working table. The block diagram and technological flow sheet were presented on Figures 1, and 2. The basic data for calculation of the material balance are: the total consumption of Cu /year is 1232.00 kg; the quality of cathode copper is 99 wt. %; the copper wt percent in finished product is 37.09 %; $CuCl_2 \cdot 2H_2O$ crystallization is 90 wt %; the total consumption of 36 % HCl /year is 3432 l and the total consumption of 65 % HNO_3/year is 1040 l.

3.1. Copper balance

The request quantity of cathode copper in dissolving process is 14 kg per charge. The high value of copper losing in waste water (9.9wt. %) is expected because the crystallization percent the first crystals is 90%. In order to achieve of high purity $CuCl_2 \cdot 2H_2O$, it is necessary to perform the second crystallization, and then the re-crystallization of obtained crystals. The copper residue in the waste water at the end of this process is 29.7 g per charge and the total recovery is 99.8 wt. %. The quality of $CuCl_2 \cdot 2H_2O$ crystal was proved by the ICP-instrumental analytical method.

Table1. The required raw material and chemicals for production the unit per 1 kg $CuCl_2 \cdot 2H_2O$

Raw material	Cathode Copper	Hydrochloric acid	Nitric acid	Distilled water	Ethyl alcohol	Electrical energy
Unit	kg	l	l	l	l	kWh
Unit/1 kg $CuCl_2 \cdot 2H_2O$	0.41	1.15	0.35	1.40	0.10	3.11

The required raw materials, chemicals and electric power, are based on the first crystals copper (II) chloride. The second crystallization products 3.65 kg $CuCl_2 \cdot 2H_2O$/charge, or $107.30 \cdot 10^{-3}$ kg (II) crystals/1 kg obtained (I) crystals of this salt. Due to the prices of: raw materials, chemicals, electric and working power, based on data presented on Table1. estimation of profitability of copper (II) chloride could be obtained. By balance of material and waste water in Cu-chloride production, the quantity and chemical composition of waste water from all process and phases are given:

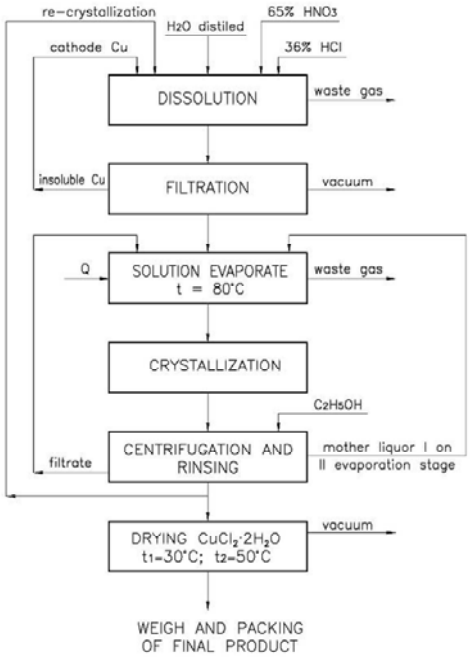

Figure 1. The block diagram of technological process $CuCl_2 \cdot 2H_2O$ production

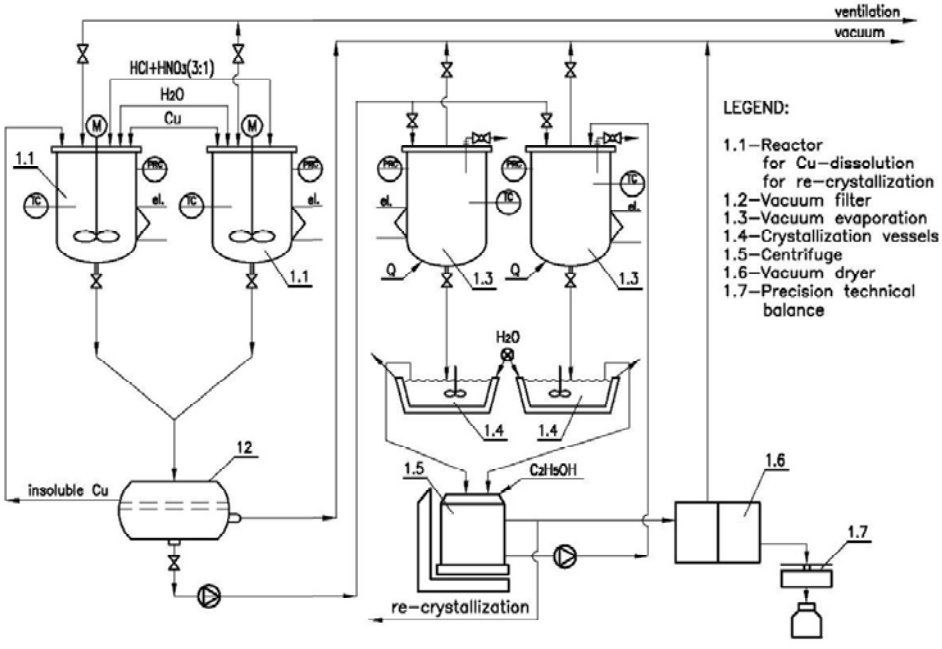

Figure 2. The flo- sheet technological process $CuCl_2 \cdot 2H_2O$ production

Waste water after the 1st crystallization:
- V_{total} = 29.10 l/charge, or 0,85 l/1 kg Cu-salt
- $Q_{Cu\text{-}chloride} = 128 \cdot 10^{-3}$kg/l waste water
- $Q_{cu} = 47.77 \cdot 10^{-3}$kg/l waste water
- $Q_{HCl(free)} = 68.73 \cdot 10^{-3}$kg/l waste water

Waste water after the 2nd crystallization:
- V_{total} = 13.50 l/charge, or 0.387 l/1kg Cu-salt
- $Q_{Cu\text{-}chloride} = 5.90 \cdot 10^{-3}$kg/l waste water
- $Q_{Cu} = 2.20 \cdot 10^{-3}$kg/l waste water
- $Q_{HCl\ (free)} = 31.85 \cdot 10^{-3}$kg/l waste water

After the first crystallization, the loss of copper has high value in waste water (1.39 kg/charge). It is necessary to evaporate a mother liquor (II).By re-crystallization it can be produce 3.65 kg of the second crystals/charge. This loss of copper, almost 10 wt % is needs to decrease by the new evaporation and after this process 13.50 l of waste water could product. This water is refined by the addition the saturated solution of NaOH or Na_2CO_3. Copper is precipitated as hydroxide and neutralizes the acid excess. The addition of NaOH produces small alkaline reaction (pH 7 – 8), and, at the end, in practical neutral water, products NaCl in total amount of 0.744 kg/charge, or $55.06 \cdot 10^{-3}$kg/l waste water. This water is cleaned by attenuation and precipitated Cu-hydroxide, partially by filtration. The total quantity of waste water from the end of the existing process can be treated in the existing system for waste water purification in The Metal Salts Plant in Bor [4]. The aggressive acid waste gasses evolve nitric oxides, calculated in NO_2 are very toxic for the health and the environmental contamination.

The chemical composition of gasses fromCu-chloride production:
- V_{NO2} = 0.95 m^3/h (during Cu-dissolving of 4h)
- $V_{CO2\ (total)}$ = 0.13 m^3/h (during Cu-precipitation of 1h)
- $V_{H2O\ (vapor).}$ = 5.45 m^3/h (during water evaporation of 12 h)

Gases from vaporization collect in a common collecting duct in which includes a digester for the crystallization $CuCl_2 \cdot 2H_2O$. The emission of CO_2 is from the waste water refining and neutralization, during of 1 h. According to discontinuous digester working, it is need to predict the possibility of disconnecting the particular digesters from the collecting gas duct.

4. CONCLUSION

By the preliminary project of the flexible plant for production copper (II) chloride, the technological line of particular copper salt is presented. In this project all need technical calculations were done, including: the material, waste water and waste gas balances. By the market request, the proposal of continuous process line is given. The material balance calculation of preliminary precise experimental investigation was presented and all technical parameters and optimal technology for $CuCl_2 \cdot 2H_2O$ production were defined.

5. ACKNOWLEDGMENT

These Researches were performed in the frame of the Project TR 34004 funded by the Ministry of Education and Science Republic of Serbia. The authors are grateful for the financial support to the Ministry.

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