

ELECTROLYTIC PREPARATION OF COPPER CARBONATE

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Electrolytic preparation of basic copper carbonates has been studied. The electrolysis was carried out both with a mixture of sodium sulphate and sodium carbonate or sodium sulphate alone with the incorporation of CO_2 , using copper electrodes or lead as cathode. The maximum current efficiency (98 percent) was obtained with the concentration of 60 g. per litre Na_2SO_4 , and at a current density of 13.5 amp./ft². 'Thur' (salinity) being abundantly available containing sodium sulphate 25-30 percent, Na_2CO_3 , 12-15 percent and NaCl, 5-7 percent provided the electrolytes. Cupric sulphate was prepared by dissolving the basic carbonate obtained from the above process in dilute sulphuric acid and crystallized out.

Basic copper carbonate (Azurite, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, or Malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ which finds a market as such, has been prepared by a number of investigators employing a variety of methods. The most important work already done being, (i) Alexander Wacker's Method: a copper gauze is immersed in a saturated solution of sodium chloride and shaken with oxygen and CO_2 at 2 atmospheric pressure, to give a precipitate of basic CuCO_3 containing 1 percent CuO , CuCl_2 , (ii) Copper is treated with oxygen in the presence of an ammoniacal solution of $(\text{NH}_4)_2\text{CO}_3$ or NH_4HCO_3 , (iii) Howard's Electrolytic Process: a solution containing NaHCO_3 or any other salt providing CO_2 and NaClO_3 is electrolyzed in the presence of a copper anode.

The conversion of electrolytic copper carbonate to copper sulphate by treatment with H_2SO_4 ensures the purity of the product. In addition, this process is much more convenient as compared to the conventional methods, i.e., treating copper scrap or ore with H_2SO_4 . This chemical finds an extensive application in textile and leather industries but the complete absence of metallic sulphates and free acid is a prerequisite.

Experimental

Electrolytic basic copper carbonates form the starting material for the preparation of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Copper carbonates best suited for the above preparation are either azurite or malachite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ or $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$). Both of these were prepared by continuous as well as batch processes.

Preparation of Electrolytic Basic Copper Carbonate.—Continuous Process: Electrolytic copper carbonates were prepared by electrolyzing a solution containing Na_2SO_4 as electrolyte, using copper electrodes or copper anode and lead cathode, while CO_2 was passed during electrolysis. Copper ions at the anode react with sulphate ions of the

electrolyte to give copper sulphate, whereas sodium ions discharged at the cathode form NaOH, which eventually gets converted to Na_2CO_3 in the presence of CO_2 . Sodium carbonate and copper sulphate so generated react together to form basic copper carbonate, i.e., azurite or malachite, regenerating Na_2SO_4 in the solution.

A series of experiments was carried out to establish most appropriate conditions for the efficient electrolysis, by varying composition and concentration of the electrolyte at various current densities.

1. *Variation of Current Efficiency* with Concentration.*—Aliquots of different concentrations of the electrolyte were electrolyzed in the presence of CO_2 at a constant current density of 13.5 amp./ft² and current efficiencies calculated in each case.

2. *Variation of Current Efficiency with Current Density.*—Taking the concentration 60 g./L. (Expt. 1, Table 1) as the optimum, the current efficiency was measured at various values of C.D. (Table 2).

The investigation covered a range of C.D. from 13.5 to 25.5 amp./ft². Current efficiency was high up to 98 percent at a C.D. of 13.5 amp./ft² but it decreased with the increase in C.D. (Fig. 1).

Instead of using CO_2 for the formation of basic copper carbonate, experiments were conducted with Na_2CO_3 in the electrolyte. The object in view was to explore the possibilities of utilizing 'Thur' which is abundantly available in saline areas of West Pakistan. The average analysis of 0.5 ton of 'Thur' collected from large area near village Chung, Tehsil Lahore, is Na_2SO_4 , 25-30%; Na_2CO_3 , 12-15% and NaCl, 5-7%. Since the composition of 'Thur' has been found to vary from place to place, the experiments were

*In the following text, the current efficiency, current density and weight g./litre are abbreviated to C.E., C.D. and g./L.

carried out by varying the composition of bath, in accordance with the varying composition of 'Thur'. This study is graphically represented in Fig. 2, wherefrom corresponding conditions can fairly be predicted.

3. *Variation of C.E. with Na₂CO₃ Concentration.*— Keeping the concentration of Na₂SO₄ constant and varying the Na₂CO₃ concentration in the electrolyte, observations were recorded. (Table 3).

It is apparent from Table 3 that the low concentration of Na₂CO₃ in the electrolyte along with Na₂SO₄ yields cupric oxide whereas basic copper carbonate is produced at higher concentrations. (Table 4).

Fig. 2 provides information about the current efficiencies with respect to the varying composition of the electrolyte.

The conversion of the basic copper carbonate used as the source for the manufacture of copper sulphate can be represented as under:

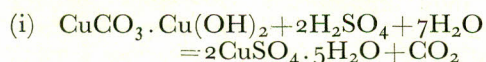


TABLE I.—VARIATION OF C.E. WITH CONCENTRATION.

No.	Na ₂ SO ₄ g./L.	Voltage (V)	Current efficiency %	Observations
1	60	2.30	98.11	Malachite
2	70	1.95	97.73	"
3	80	1.90	96.77	"
4	90	2.10	96.15	"
5	100	2.10	95.77	"

Time = 3 hours, C.D. = 13.5 amp./ft.²

TABLE 2.—VARIATION OF C.E. WITH C.D.

No.	Current amps.	C.D. amp./ft. ²	Voltage (V)	C.E. %	Observations	% composition		
						CuO	CO ₂	H ₂ O
1	0.9	13.5	2.30	98.11	Malachite	70.01	19.77	10.22
2	1.0	15.0	2.35	89.58	"	69.92	19.20	10.88
3	1.1	16.5	2.45	79.82	"	70.57	17.93	11.50
4	1.2	18.0	2.50	74.02	"	70.00	18.98	11.02
5	1.3	19.5	2.75	70.40	"	69.88	19.32	10.80
6	1.4	21.0	3.10	64.19	"	70.00	19.50	10.50
7	1.5	22.5	2.90	60.66	"	69.90	19.66	10.44
8	1.6	24.0	3.40	56.43	"	70.01	19.19	10.80
9	1.7	25.5	3.00	51.73	"	69.58	19.42	11.00

Time = 3 hours; Na₂ SO₄ concentration = 63 g./litre.

The precipitated basic copper carbonate was filtered and repeatedly washed with water till free from Na₂SO₄. As the quantity of CuCO₃

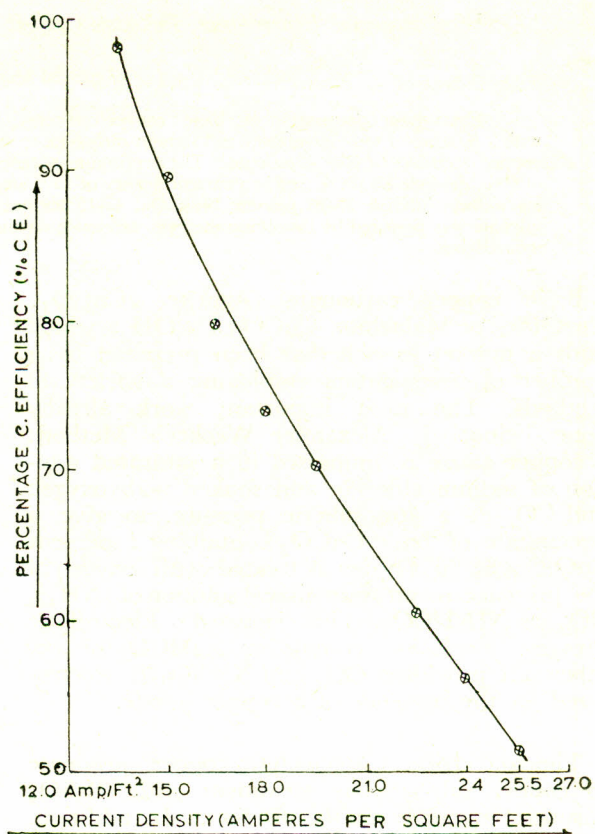


Fig. 1.—Showing variation of current efficiency with current density.

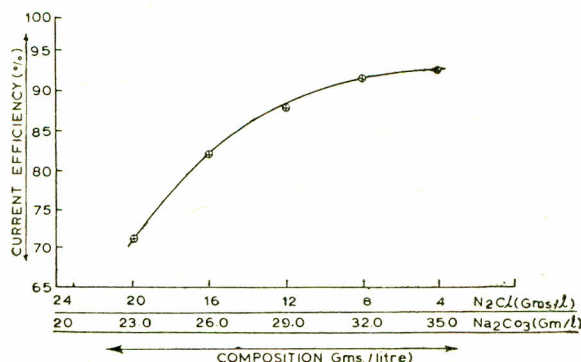


Fig. 2.—Showing variation of current efficiency with composition of the bath.

TABLE 3.—VARIATION OF C.E. WITH Na₂CO₃ CONCENTRATION.

No.	Na ₂ CO ₃ (g./L.)	C.D. amp./ft. ²	Voltage (V)	Time (hrs.)	C.E. %	Observations	Percent composition		
							CuO	CO ₂	H ₂ O
1	17.0	12.0	2.10	1.5	90.05	Black CuO	97.45	1.40	1.15
2	20.0	12.0	2.05	1.0	92.20	Malachite	69.87	20.00	10.13
3	23.0	12.0	2.25	1.5	90.29	Black CuO	96.82	1.98	1.20
4	26.0	12.0	2.25	1.5	94.40	Azurite	72.55	22.20	5.25
5	29.0	13.5	2.40	1.5	94.83	„	74.00	20.90	5.10
6	32.0	13.5	2.45	1.5	94.24	„	69.54	25.24	5.22
7	35.0	13.5	2.45	1.5	94.95	„	72.50	22.22	5.30

Average Na₂SO₄ concentration = 60 g./litre.

TABLE 4.—VARIATION OF C.E. WITH COMPOSITION.

No.	Na ₂ CO ₃ g./L.	NaCl g./L.	Voltage (V)	C.E. %	Observations
1	23.0	20.0	2.18	71	Malachite
2	26.0	16.0	2.20	82	„
3	29.0	12.0	2.35	87.72	„
4	32.0	8.0	2.35	91.25	„
5	35.0	4.0	2.30	92.17	Azurite

Average Na₂SO₄ concentration 60 g./litre; C.D. 12 amp./ft.²

and Cu(OH)₂ varied from batch to batch, it was considered appropriate to dissolve the basic copper carbonate (malachite or azurite) in a slightly lesser volume of H₂SO₄ (40%). The remaining basic complex was allowed to settle and the solution was decanted off. This procedure ensured the purity of copper sulphate, as no free acid was left to contaminate. The remaining basic copper carbonate was then recycled.

Discussion

The experimental work detailed out above leads to the fact that maximum yield of copper carbonate can be obtained at the optimum conditions, i.e., at the C.D. of 13.5 amp./ft.² and 60 g./

litre concentration of Na₂SO₄. The incorporation of CO₂ is also of vital importance as the decrease of the carbonate content facilitates the decomposition of basic copper carbonate to CuO, which adversely effects the yield of basic carbonate, and substantially minimizes the efficiency of the bath. It is, therefore, evident that suitable maintenance of all these relevant factors is very essential. Another important factor worth mentioning is that no special material of construction is required to carry out this process. On the basis of the experimental work, it can safely be mentioned that the most suitable bath can be of lead, which also functions as a cathode.

The basic copper carbonate can easily be converted to copper sulphate by treatment with

dilute sulphuric acid. The copper sulphate, as already discussed earlier will be free from sulphuric acid. The process can be made further economically feasible by utilizing the CO₂ which is liberated during the acid treatment.

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