Management of a copper smelter dust for copper profitability

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Abstract

A flue dust sample of copper from a smelter furnace has been used as a source for copper recovery. The main phases of the dust are: chalcocyanite, maghemite, sinnerite and copper-molybdenum oxide. The leaching of the flue dust sample with ammonium carbonate solutions dissolved most of the non-metallic copper species, in an endothermic process, i.e.:

$$CuSO_4 + (NH_4)_2CO_3 \rightarrow Cu(NH_3)_2^{2+} + SO_4^{2-} + CO_3^{2-} + 2H^+$$

remaining most of the others metals in the solid due to the alkaline pH value of the resulting solution.

From the near pure copper(II) solution, this metal is cemented with metallic zinc:

$$Cu^{2+} + M^0 \rightarrow Cu^0 + M^{2+}$$

where M represented the cementation agent.

Another route to recover copper(II) is by means of liquid-liquid extraction technology using oximes, cetoximes or β-diketones as organic extractants for copper(II). Firstly, copper(II) is extracted accordingly with the next equilibrium:

$$Cu(NH_3)_{2_{aq}}^{2+} + 2HR_{org} \Leftrightarrow R_2Cu_{org} + 2NH_{4_{aq}}^{+}$$

where the subscript org and aq refereed to the respective organic and aqueous phases and HR to the extractant. The advantage here is that in this ammoniacal medium, the protons released in the conventional extraction process:

$$Cu_{aq}^{2+} + 2HR_{org} \Leftrightarrow R_2Cu_{org} + 2H_{aq}^{2+}$$

are fully neutralized by ammonia from the copper(II)-ammonia complex. Then, a second step or stripping step is necessary to release the extracted copper(II) to a new aqueous solution:

$$R_2Cu_{org} + H_2SO_{4_{aq}} \Leftrightarrow 2HR_{org} + Cu_{aq}^{2+} + SO_{4_{aq}}^{2-}$$

regenerating the extractant and yielding a pure copper(II) sulphate solution which can enter an electrowinning operation to yield grade A copper cathode.

With the two solutions, a saleable product, copper cement or copper cathode, is obtained.

Keywords: copper flue dust, ammonium carbonate, leaching, cementation, liquid-liquid extraction, metallic zinc, LIX 54.

1.INTRODUCTION

The production of copper dusts is inherent with all the furnaces types used in the copper pyrometallurgy. This copper dusts has an important amount of various forms of copper compounds (even metallic copper) together with a number of elements accompanying to copper in the raw materials, and if the recycling of the dusts to the furnaces is an option, is also desiderable to investigate hydrometallurgical processing options to recover copper from the dusts and render them as safe residuals. Thus, several processes had been claimed having in mind this first idea [1-7], among the leachants, the leaching with ammonium salts may be an option due to the facility from which copper(II) is stabilized in the aqueous solution as the corresponding ammine-copper(II) complexes and because the resulting solutions are practically free of non-desired elements, since they are remaining in the solid residue due to the alkalinity of the solutions.

In the present investigation, a sequential process of a Chilean copper flue dust is given, based in two practical options: *i)* leaching with ammonium carbonate solutions and *iia)* cementation of copper from the solution using metallic zinc or *iib)* liquid-liquid extraction of copper using LIX 54 (β-diketone derivative) as extractant and sulphuric acid as strippant. In case *iia)*, cement copper is the final product, whereas in the *iib)* option the final product should be copper cathode.

2.EXPERIMENTAL

2.1.Materials

The dust from the flash furnace of a Chilean copper smelting plant is collected by electrostatic filters and is relatively fine (Figure 1), some defined spherical-shaped particles can be observed together with irregular ones, all with various sizes. The XRD characterization of the flash flue dust sample indicates the complexity of this copper (in general all) flue dusts. It consists mainly in oxidized species (chalcocyanite ($CuSO_4$), maghemite (Fe_2O_3), sinnerite (Cu_6As_4), complex Cu-Mo oxide) with a few sulfide species, though the presence of amorphous species, which were not identifiable by

XRD, may be considered. The composition of the flash dust is shown in Table 1, it is evident the richness in copper that this flue dust presents.

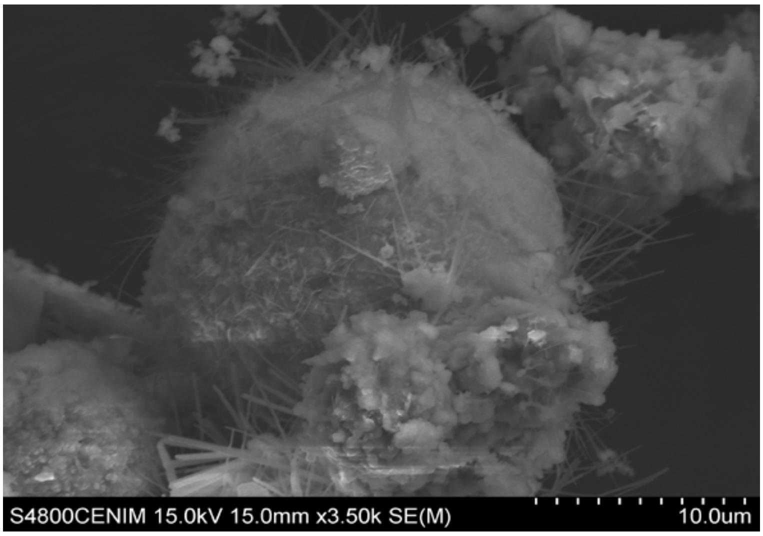

Figure 1. SEM image of the flue dust. The as-needles forms are rich in iron and arsenic.

Table 1. Main elements of the flash flue dust

	Copper	Iron	Molybdenum	Lead	Aluminium	Arsenic	Zinc
% wt	24.5	14.0	0.45	0.08	1.2	0.9	0.15

LIX 54 extractant was used as supplied by the manufacturer (Cognis). The active substance of the reagent is a β-diketone, which basic structure can be represented by R-CO-CH$_2$-CO-R´ (where R and R´ represent alkyl chains). Iberfluid (CS) a kerosene type diluent containing more than 98% aliphatics, boiling range 210-284º C and flash point 96º C, was used as diluent for LIX 54.

All other reagents used in the present investigation were of AR grade, and metals were analysed either by AAS or ICP-MS.

2.2.Procedures

Leaching experiments have been carried out in a 1 liter autoclave and in the basis of mild conditions, principally to reduce energy costs.

Cementation experiments were done in a glass reactor provided of mechanical shaking (impeller). All the experiments were carried out using a stirring speed of 300 min^{-1}.

Solvent extraction experiments were performed both in batch and continuous conditions. Batch tests were carried out in water jacketed 100 mL separatory funnels provided with mechanical shaking and thermostatted at the required temperature (20º C unless otherwise stated) and organic:aqueous phases relationship of 1:1, whereas continuous investigations were conducted in a 2-4 cell water jacketed mixer-settler unit, also thermostatted at the required temperature and mechanically shaken. The unit had various flow capacities for each phase (maximum 100 mL/min), whereas mixing and settling volumes were 200 and 700 mL, respectively.

3.RESULTS AND DISCUSSION

3.1.Leaching

Leaching or dissolution is the first operation (after the preparation of the material to be treated) of Hydrometallurgy. This operation referred to the process of recovering a metal from the material containing it by a lixiviant or leachant using aqueous solutions. Thus, this process of solubilization of the constituents of a given material to form a solution is a solid-liquid mass transfer process. Various operational variables can occur, but generally the leaching reagent must fulfil all of as many as possible of the next considerations: *i)* it must dissolve the targeted metal as rapidly as possible to make commercially feasible the operation, and it should no attack the non-desiderable elements or gangue of the starting material, *ii)* it may be cheap and readily obtainable in large amounts, *iii)* it is better that it can be regenerated within the whole process.

Probably, ammonium carbonate fulfils most if not all of the above requirements. The results derived from leaching experiments, using ammonium carbonate solutions and various experimental variables, on the copper flue dust are summarized in Table 2.

From this series of experiments it can be deduced that under the various experimental conditions investigated the percentage of copper dissolved, around 80 %, is not sensitive with the variation of the ammonium carbonate concentration in the starting solution. Other conclusions derived from the above table is that the variation in the L/S ratio does not affect to the percentage of copper dissolved when concentrated ammonium carbonate solutions are used to leach the flue dust, however, when dilute salt solutions were used, the percentage of copper leached drops dramatically as the initial L/S ratio decrease, this is due to the decrease of the number of ammonia ligands available per copper atom (see below), which results in the no solubilization of the metal. It should also worth to be mentioned here that practically the same results are obtained when reaction times of 1-2 h are used.

Table 2. Leaching of copper flue dust using ammonium carbonate solutions.

Ammonium carbonate, g/L	L/S ratio	pH	% Cu leached	Cu in solution, g/L
260	100	8..6	79.6	1.95
130	100	8.7	82.4	2.02
65	100	8.7	81.2	1.99
260	100	8.6	79.6	1.95
260	10	8.5	79.9	19.6
65	200	8.8	92.2	1.13
65	100	8.7	81.2	1.99
65	20	7.8	45.1	5.5
65	10	7.3	9.8	2.4

Time: 30 min. L: mL of solution. S: g of flue dust

Besides the above, the most important feature of the leaching results is the higher copper concentrations which can be yield in the solutions after leaching with ammonium carbonate solutions, and the characteristics of the operation derived with the use of ammonium salts [8]. Due to the weak acidic nature of the ammonium ion, the next reaction takes place:

$$NH_4^+ \Leftrightarrow NH_3 + H^+ \qquad (1)$$

and the resultant ammonia forms highly stable complexes with copper (II) ($Cu(NH_3)_n^{2+}$, n: often 2 or 4), increasing the dissolution power of this leaching medium. Also, the leaching with ammonium carbonate solutions normally runs at near constant and near neutral or slightly alkaline pH value range. Despite the above equation and the generation of ammonia, the pH of the solution does not vary appreciably since most of the generated ammonia is complexed by copper (II), while the uncomplexed ammonia and the ammonium salts resulting in a buffer system which maintained the pH of the solution almost fixed. Being this pH slightly alkaline, the solution obtained from the leaching operation is very pure, having very low values (in the range of few mg/L) of other impurities found in the flue dust and free of iron, which remained in the residue probably as an iron (III) oxide species.

3.2.Cementation

Cementation is an older hydrometallurgical operation but still useful today, as the recovery of several metals (i.e. copper, gold, cadmium) using the technology demonstrated. In cementation operation, one metal M_A is precipitated to its zero valence state from its aqueous solution by the addition of a second metal M_B, in its zero state, to the solution. The overall reaction representing the above process is:

$$M_A^{n+} + M_B^0 \rightarrow M_A^0 + M_B^{n+} \qquad (2)$$

The choice for the metal to be used as cementation agent is dictated by the relative position of both metals A and B in the electromotive force (EMF) series, thus, those metals occupying higher positions (more positive oxidation potentials) in the series can be used to precipitate metals occupying lower positions (more negative oxidation potentials) in the series. The larger the difference between these two values, the better to obtain a good yield in the operation.

In the particular case of copper, the cementation of the metal from acidic solutions, using scrap iron, is a well used industrial operation to obtain metallic copper. However, in the case of alkaline solutions as these obtained in Section 3.1., metallic iron, in whatever form, is not the choice to cement copper, instead metallic zinc can be used to cement copper according with the overall reaction:

$$Cu^{2+} + Zn^0 \rightarrow Cu^0 + Zn^{2+} \qquad (3)$$

with standard free energy change of $\Delta G_{298}^0 = -35.19 - 15.54 = -50.73 \text{kcal}$.

The pH of the aqueous solution has an influence on the cementation of copper(II) by metallic zinc, as results given in Figure 2a shown. It can be seen that copper(II) is well cemented from solutions of pH 4, but very bad precipitated from ammoniacal alkaline solutions. However, this situation can be remediated if the aqueous solutions contained excess of ammonia ligands and the pH of the solutions is maintained in the 8-9 range. In the present case, and being ammonium carbonate the leachant for the copper flue dust, the same salt was used in the cementation studies of copper(II).

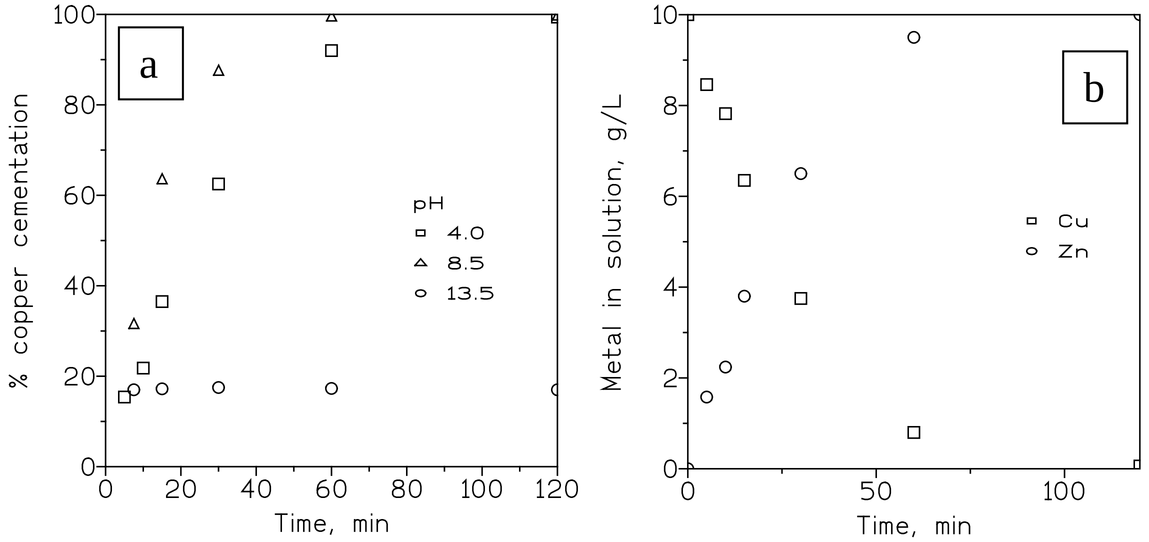

Figure 2a. Influence of pH on copper cementation. Aqueous solution: 10 g/L copper at the desired pH (the solution at pH 8.5 also contains 260 g/L ammonium carbonate). Zn/Cu molar relationship: 2. Temperature: 20º C.

Figure 2b. Metal concentrations profiles in the aqueous solutions for experiments carried out with the solution of pH 4. The same pattern is obtained with solutions of pH 8-9 containing ammonium carbonate.

Figure 2b showed the metal concentrations profiles in the solution during the cementation process. At the end, the molar relationship Zn in solution/Copper cemented is nearly 1, which corresponded well with the stoichiometry described by equation (3).

Table 3 shows the effect of adding this salt to the aqueous solution in the 260-65 g/L range at pH 8-9. It can be seen the effectiveness that the presence of this salt in the aqueous solutions has on the percentage of copper cementation by powdered zinc.

However, the cementation of copper is viable at 65 g/L ammonium carbonate if an excess of cementing agent is added to the solution, as results in Table 4 shown. These results shown that when the initial Zn/Cu molar relationship is increased, the percentage of copper cemented is increased, obtaining a complete or near complete copper precipitation at an initial Zn/Cu molar relationship of 4 to 8. In the case of solutions containing 260 g/L ammonium carbonate, the same tendency as above is observed, but complete copper cementation is obtained at initial Zn/Cu molar relationships of 1.5.

Table 3. Influence of ammonium carbonate on copper(II) cementation.

Ammonium carbonate, g/L	15 min	30 min	60 min
65	13.1	13.3	13.5
89	34.5	46.4	44.7
113	65.0	86.8	97.4
160	91.0	99.1	>99.5
210	65.2	91.8	>99.5
260	68.5	87.5	>99.5

Aqueous solution: 10 g/L copper in ammonium carbonate, pH 8.5±0.02. Zn/Cu molar ratio: 2. Temperature: 20º C

Table 4. Influence of the Zn/Cu molar relationship on copper(II) cementation.

Zn/Cu	15 min	30 min	60 min	2h
8	84.2	95.0	99.5	>99.5
6	53.2	63.6	80.5	98.3
4	48.5	61.1	73.0	97.6

Aqueous solutions: 5 g/L copper and 65 g/L ammonium carbonate, pH 8.5. Temperature: 20º C

In all the above cases, zinc(II) in solution is stabilized as the corresponding ammoniacal complexes $Zn(NH_3)_n^{2+}$.

The morphology of the cements is shown in Figure 3.

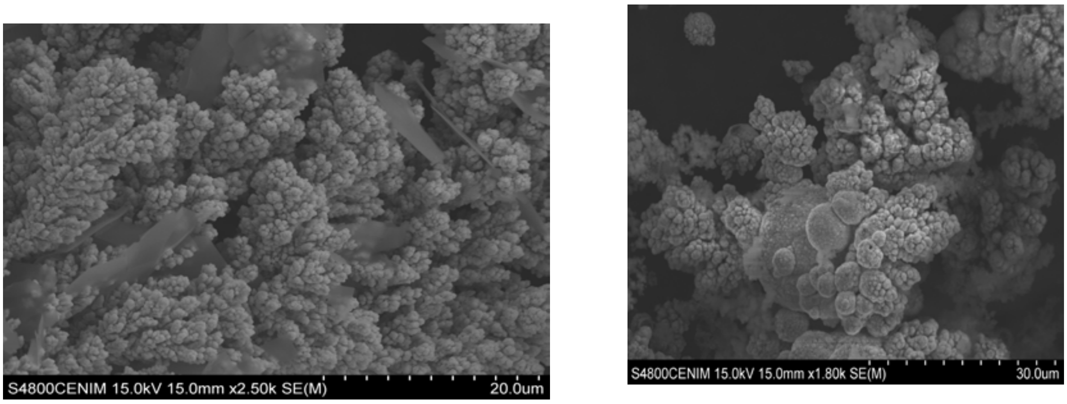

Figure 3. SEM images of copper cemented, at pH 4 (left) or at pH 8.5 in 160 g/L ammonium carbonate medium (right), on zinc.

In both cases, the copper cemented has the form of granular particles or globules, whereas unreacted zinc is represented by the non-granular or smooth specimens.

3.3.Liquid-liquid extraction

Too much dilute copper(i.e. below 5 g/L) or complex solutions result unpractical for direct production of copper cathodes. In theses cases, liquid-liquid extraction is the technology which ensures the production of lean copper(II) solutions and with the adequate copper concentration to allows their direct feeding to the electrowinning plant to yield as saleable product, grade A copper cathode [9].

The operation consists in two steps, one for the metal extraction and the second for metal stripping from loaded organic solutions. The extraction of copper responded to the next general equilibrium:

$$\mathrm{Cu^{2+}_{aq} + 2HR_{org} \Leftrightarrow R_2Cu_{org} + 2H^{2+}_{aq}} \qquad (4)$$

where HR represented the active substance of the extractant or organic reagent. If the equilibrium is shifted to the right, copper(II) is extracted to the organic phase, and if the equilibrium is shifted to the left, copper(II) is unloaded from the organic phase. Thus, copper(II) results from an aqueous solution of low acidity to an aqueous solution of high acidity.

In the case of copper(II) liquid-liquid extraction operation, the extractants (HR) most widely used in practice are ketoximes, salicyalaldoximes, tailored mixtures of both types of extractants and β-diketones (these are suited to the processing of highly ammoniacal copper(II) solutions).

As it is mentioned in the Abstract section, in the present case, eq.(4) is replaced by:

$$\mathrm{Cu(NH_3)^{2+}_{2_{aq}} + 2HR_{org} \Leftrightarrow R_2Cu_{org} + 2NH^{+}_{4_{aq}}} \qquad (5)$$

as extraction step, and

$$\mathrm{R_2Cu_{org} + H_2SO_{4_{aq}} \Leftrightarrow 2HR_{org} + Cu^{2+}_{aq} + SO^{2-}_{4_{aq}}} \qquad (6)$$

as stripping step. In the case of extraction, the formation of the diammine-copper(II) complex as product of the leaching step, results in the neutralization of the protons released to the aqueous solutions as consequence of copper extraction, and regenerating the leaching reagent. In the case of the stripping step with a sulphuric acid solution (i.e. 160-180 g/L H_2SO_4), this solution represented to the spent electrolyte exiting the electrowinning operation, whereas the aqueous copper solution (right hand side of eq.(6)) represented the advanced electrolyte to feed the electrowinning plant.

Preliminary experiments were carried out in order to determine the time needed to achieve equilibrium. From this study using 10% v/v LIX 54 in Iberfluid as organic phase and an aqueous solution of 2 g/L copper in 65 g/L ammonium carbonate at pH_{eq} 8.5±0.02, the results obtained showed that equilibrium is reached within 2.5 min of mixing, with a percentage of metal extraction of 98.9, whereas increasing temperature (10-50^o C) gave an increase in copper extraction, thus indicating an endothermic reaction.

Using the same solutions as above, the effect of increasing the concentration of ammonium carbonate in the aqueous solution on copper extraction was also investigated. Increasing this concentration in the aqueous solution results in a decrease of the percentage of copper extraction, from 98.9 to 80.3 for ammonium carbonate solutions in the 65 to 260 g/L range, respectively. This means that at higher ammonium carbonate concentrations more stages are needed to completely extract copper from the aqueous feed.

Results studying the maximum loading capacity of the extractant, had shown that this value (5 g/L for 10% v/v LIX 54 in Iberfluid) remained unaltered despite the presence in the aqueous solution of ammonium carbonate concentrations in the range used in this work.

Since, copper(II) is not extracted by LIX 54 at pH values below 3, the use of copper spent electrowinning solutions (160-180 g/L sulphuric acid) ensured the strip of the metal from the loaded organic phase to the aqueous solution which represented the advanced electrolyte.

Counter-current extraction in the mixer-settler unit containing one extraction stage and two stripping stages were carried out to test the performance of the system in a continuous basis. In this context, a feed solution containing 2 g/L Cu (II) and 65 g/L ammonium carbonate at pH 8.5±0.02 was extracted by a 10 % v/v solution of LIX 54 Iberfluid at a phase ratio of 2:1 (aqueous: organic); a 30 g/L copper(II) and 170 g/L sulphuric acid solution (spent electrolyte) was used as the strip phase using a phase ratio of 1:1. The conditions and results used in the counter-current run are showed in the flow-sheet given in Figure 5. After 100 hours run operation an average 99.5 % of copper extraction and 99.9 % copper stripping (advanced electrolyte: 33.9 g/L Cu and 163 g/L sulphuric acid) are achieved.

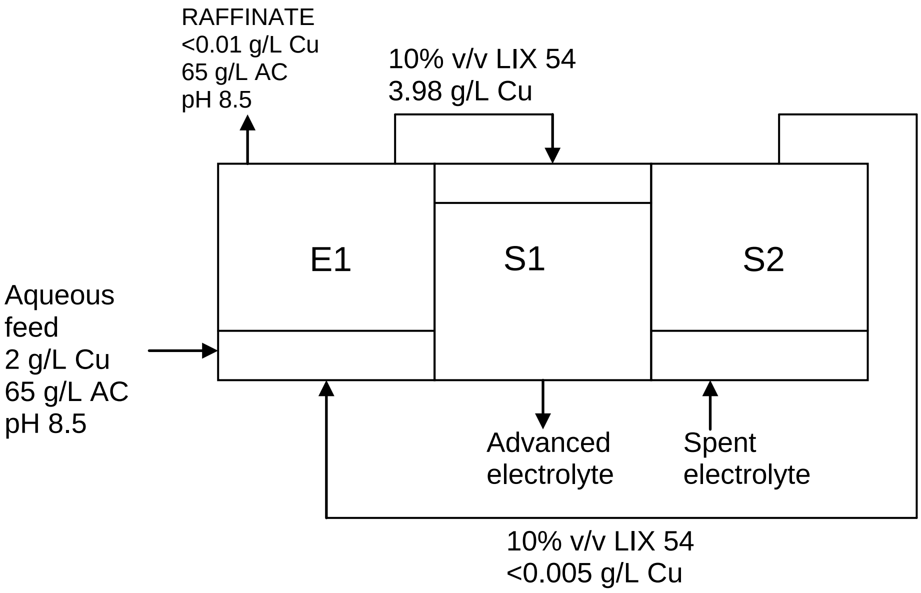

Figure 4. Schematic flow-sheet for the treatment of the copper solution *via* solvent extraction technology. AC: ammonium carbonate. E1: extraction stage. S1 and S2 stripping stages.

4.CONCLUSIONS

The use of ammonium carbonate solutions allowed to the dissolution of copper from copper flue dusts, but probably if this element is not present in the dust as metallic copper and/or sulphides. Besides copper, the metal-lean solutions obtained from the leaching operation can be processed *via* cementation or liquid-liquid extraction to yield two saleable copper products.

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