

Sulfur Dioxide: A Versatile Reagent for the Processing of Cobaltic Oxide Minerals

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Cobaltic oxide minerals are readily dissolved in mildly acidic sulfuric solutions provided a reducing agent is also present. Sulfur dioxide is the most common reductant recommended for this purpose, but its addition during the leaching step could lead to significant environmental problems and could affect the recovery of copper if present in large amounts. This paper presents a novel approach whereby the reductant used during the leach is ferrous sulfate and sulfur dioxide is added at a later stage in a controlled manner to regenerate the reductant after any copper present has been recovered. Sulfur dioxide can also be used during purification of the cobalt bleed, where, blended with oxygen, it constitutes a powerful oxidant capable of selectively oxidizing and precipitating manganese away from the cobalt. This paper will present several applications of the use of sulfur dioxide as a primary reductant, a regenerant for ferrous sulfate, and a selective oxidant for manganese.

INTRODUCTION

Historically, primary cobalt has been mostly recovered as a by-product of the copper and nickel industries. For many decades, a significant portion of the world's primary cobalt originated from the Central Africa Copper Belt, more particularly from the Democratic Republic of Congo (DRC, formerly known as Zaire).

In the DRC Gecamines plants, cobalt sulfide (mostly carrollite CuCo_2S_4) was recovered by flotation. In its oxide form, cobalt is present as cobaltous (mostly sphaerocobaltite CoCO_3), but mostly as cobaltic mineral. The most abundant cobaltic mineral is heterogenite, named stannierite $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ in its fully crystallized form, more generally

$\text{CoO} \cdot 2\text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ in its amorphous form. Cobaltic minerals also frequently occur as a cobaltiferous wad ("asbolite") in a mixture with manganese and iron oxides. Similar associations are also encountered in manganeseiferous sea and land nodules,¹ and in nickel laterites.²⁻⁶

Cobaltic oxide minerals are fairly refractory in mildly acidic solutions, as are manganic oxide minerals. As manganic oxides, they require a reducing environment to undergo dissolution.

Sulfur dioxide is a very common reductant produced in large quantities during the roasting and smelting of sulfides. It has been suggested for use as a primary reductant for manganic oxide minerals and therefore for cobaltic oxide minerals. However, sulfur

dioxide is a fairly versatile reagent that can find several applications during the treatment of cobaltic minerals: it can be used also as secondary reductant after the leach and as an oxidant (in a gas mixture) for the selective precipitation of iron and manganese during the purification of cobalt solutions.

This paper presents various uses of sulfur dioxide during the treatment of cobaltic oxide minerals, the underlying chemistry, and examples of applications.

COBALTIC OXIDE ORE SAMPLES TESTED

Ore samples of various types and origins have been investigated during this study. Table I presents their chemical analyses. Samples A, B, and C originated from Central Africa and represent sedimentary copper-cobalt siliceous ores with copper mainly as malachite. Sample D originated from Central America while sample E, originating from West Africa, represented a nickel-cobalt lateritic ore.

All these samples contained the cobalt in the cobaltic form, with usually less than 20% of the cobalt soluble in mildly acidic solutions. As an example, Figure 1 presents the results of an agitation leach carried out on sample A ground to a P_{80} of 80 μm .

Copper dissolution in acid solutions was excellent (95% in 45 minutes), as expected from malachite. Cobalt dissolution was limited to less than 10% due to the refractory nature of cobalt (III) under those conditions.

SULFUR DIOXIDE AS A PRIMARY REDUCTANT

It has long been known that sulfur dioxide could be used effectively as a reductant during acid dissolution of py-

How would you...

...describe the overall significance of this paper?

This paper documents several improvements/modifications to the hydrometallurgy of cobalt by the diverse application of a common chemical, sulfur dioxide.

...describe this work to a materials science and engineering professional with no experience in your technical specialty?

It shows that the same common chemical (sulfur dioxide) can be used in various applications during the same process to achieve different goals and optimize the process.

...describe this work to a layperson?

This work shows that some creativity and a sound knowledge of basic chemistry gives the metallurgist flexibility to optimize the metallurgy of cobalt by using the same common chemical (sulfur dioxide) in various areas of the process.

rolusite MnO_2 ores.⁷ By analogy, sulfur dioxide has also been suggested as a primary reductant during acid dissolution of cobaltic ores.⁸ It is suggested⁹ that the reductive dissolution of heterogenite occurs as per the reaction:

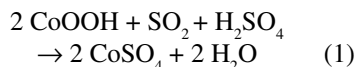


Figure 2 confirms the dissolution of cobalt (and manganese) when adding sulfur dioxide during the column leach of sample E. Sulfur dioxide was added as sodium metabisulfite to the leach solution. Similarly, when gas SO_2 was added (80 kg SO_2/t) to sample A under otherwise the same conditions as those presented in Figure 1, cobalt extractions

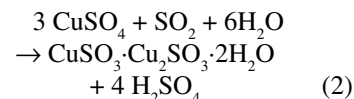
Table I. Chemical Analyses of Cobalt Ores/Concentrates used in the Study (%)

	A	B	C	D	E
Cu	9.9	4.8	5.1	0.43	<0.01
Co	1.8	0.43	0.43	0.07	0.75
Fe	1.8	1.8	1.8	7.94	36.0
Mn	<0.05	<0.05	<0.05	4.49	1.62
Ni	—	<0.003	<0.003	0.01	0.80

increased to 94.7% in 2 hours. These results confirmed the effectiveness of sulfur dioxide as a primary reductant for cobaltic oxides.

However, the use of SO_2 presents several major drawbacks. The most obvious relates to the environmental and health risks associated with gaseous SO_2 emissions and almost precludes its use in heap or vat operations.

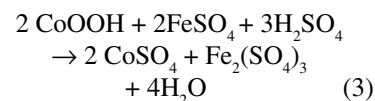
Another drawback is metallurgical, as illustrated in Figure 3. The results in that figure confirm the positive effect of sulfur dioxide additions on cobalt extraction but also a significant drop of copper extraction at higher SO_2 additions, likely due to the precipitation of Le Chevreult's salt, as per the reaction:



This potential side precipitation of a copper sulfite salt represents a significant danger of losing metal values.

SULFUR DIOXIDE AS A SECONDARY REDUCTANT

As an alternative to using SO_2 as a reductant during the leaching stage of cobalt oxide ores, it has been suggested to add ferrous sulfate in the leach solution.^{9,10} By analogy with manganese ores,¹¹⁻¹⁴ it is assumed that the chemistry of the reductive leach follows Reaction 3:



Confirmation of the concept is presented in Figure 4 for the same ore type A as used in Figures 1 and 3. Results in Figure 4 confirm the suitability of using ferrous sulfate instead of sulfur dioxide at the leach stage; it also demonstrates that excess reductant does not have a negative impact on copper recovery since the conditions for copper sulfite

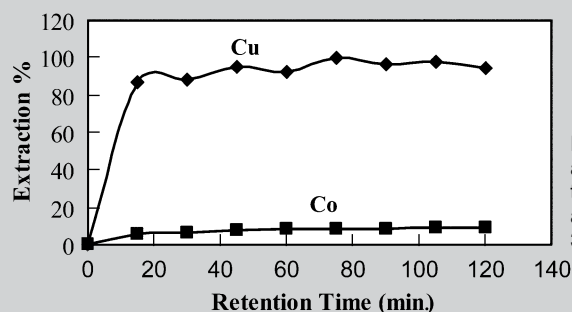


Figure 1. The kinetics of copper and cobalt dissolution from ore type A when using only sulfuric acid: pH ~1.9; temperature = 33°C; $P_{80} = 80 \mu\text{m}$.

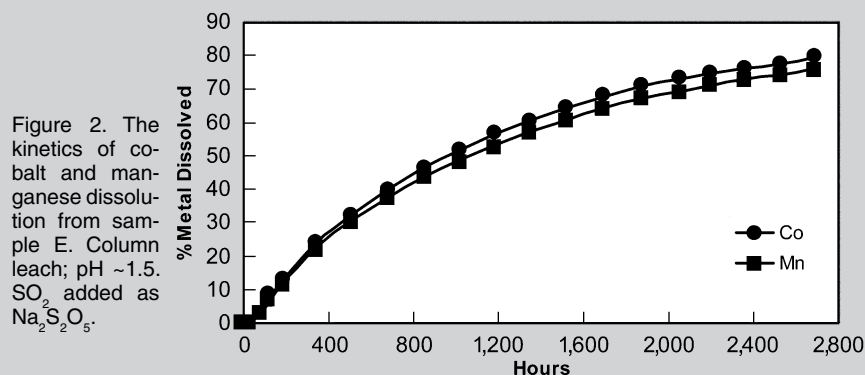


Figure 2. The kinetics of cobalt and manganese dissolution from sample E. Column leach; pH ~1.5. SO_2 added as $\text{Na}_2\text{S}_2\text{O}_5$.

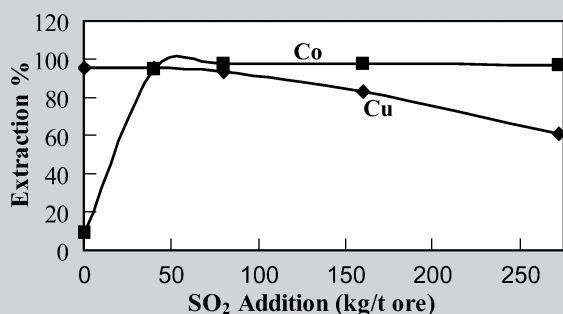


Figure 3. The effect of SO_2 addition on copper and cobalt extraction from ore type A. Temperature: 33°C; pH ~1.9; $P_{80} = 8 \mu\text{m}$; retention time: 120 min.

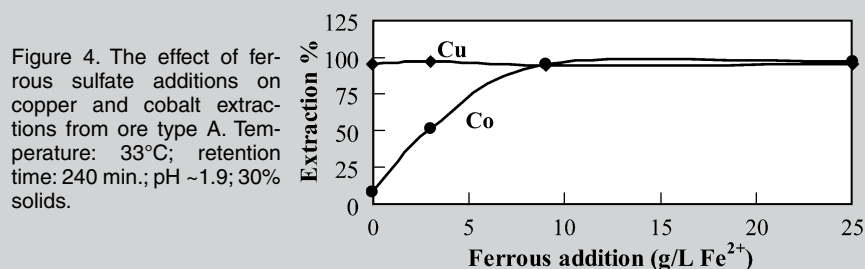


Figure 4. The effect of ferrous sulfate additions on copper and cobalt extractions from ore type A. Temperature: 33°C; retention time: 240 min.; pH ~1.9; 30% solids.

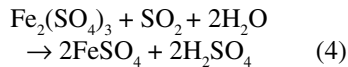
precipitation do not exist.

The reductant being already dissolved, the efficiency of the reduction does not depend on a gas phase mass transfer and the kinetics of cobalt reductive dissolution are fairly rapid, as shown in Figure 5.

The dosage of ferrous sulfate needed in solution will depend on various factors, and under the proper conditions, cobalt extractions higher than 90% could be obtained in 4 hours. As expected, and as was the case when using SO₂ (see Figure 2), any manganic oxides in the ore would also be reductively leached with ferrous sulfate, as shown in Figure 6. Under the conditions of the leach, without a reductant, about 44% of the manganese and 58% of the cobalt are acid soluble. The addition of ferrous sulfate brings manganese recovery practically to completion (97.5%), while that of cobalt is increased by 20%.

It is usually desirable to regenerate the reductant, not only to lower the operating costs, but also to minimize the concentration of iron in the cobalt leach solution prior to the subsequent cobalt recovery/purification circuit.

A convenient method would be to reduce the ferric sulfate (resulting from Reaction 3), as per the well-known Reaction 4, using sulfur dioxide as a secondary reductant:



The extent of the reduction is conveniently monitored by measuring the solution oxidation reduction potential (ORP). Examples of application are presented in Figure 7 for various SO₂ flow rates and a 1L solution containing 12 g/L Co, 1.5 g/L Cu, 26 g/L H₂SO₄, and 6.8 g/L Fe³⁺.

The reduction of ferric sulfate with SO₂ gas was rapid and completed in less than 1 hour at the higher flowrate. The reduction of the ferric ion is more efficient if carried out from a solution instead of a pulp. One of the major advantages of using ferrous sulfate as a primary reductant during the leach, and sulfur dioxide as a secondary reductant to regenerate the ferrous sulfate at a later stage, is the opportunity of applying this process to heap and vat leaching.

In those situations, the leach solution

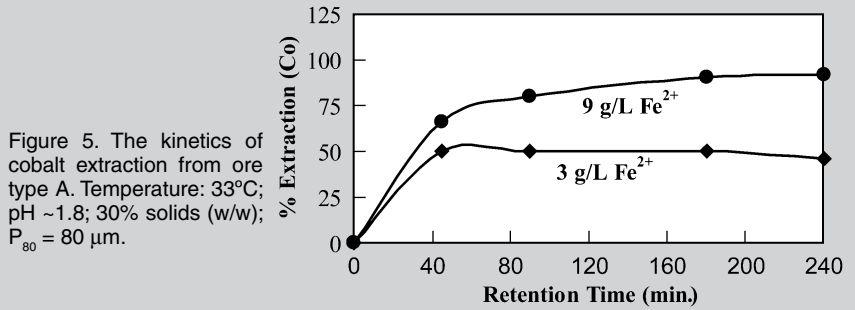


Figure 5. The kinetics of cobalt extraction from ore type A. Temperature: 33°C; pH ~1.8; 30% solids (w/w); P₈₀ = 80 μm.

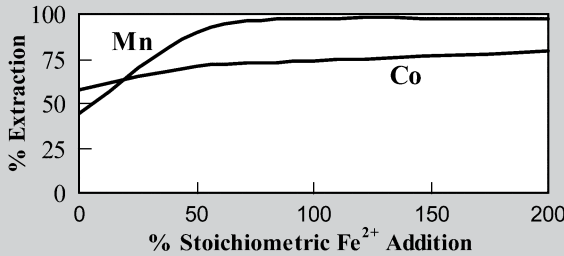


Figure 6. The extraction of cobalt and manganese from ore type D as a function of the stoichiometric (Mn + Co) Fe²⁺ ion addition. Temperature: 50°C; pH ~1.5.

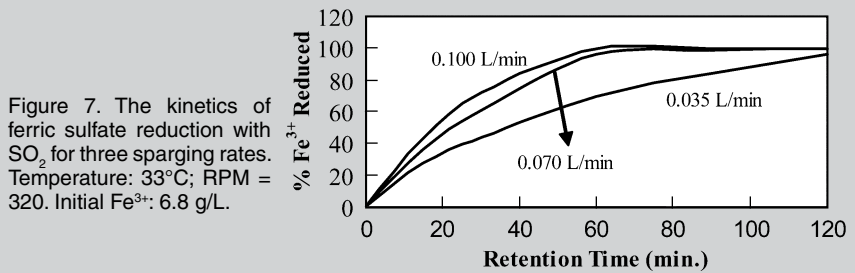


Figure 7. The kinetics of ferric sulfate reduction with SO₂ for three sparging rates. Temperature: 33°C; RPM = 320. Initial Fe³⁺: 6.8 g/L.

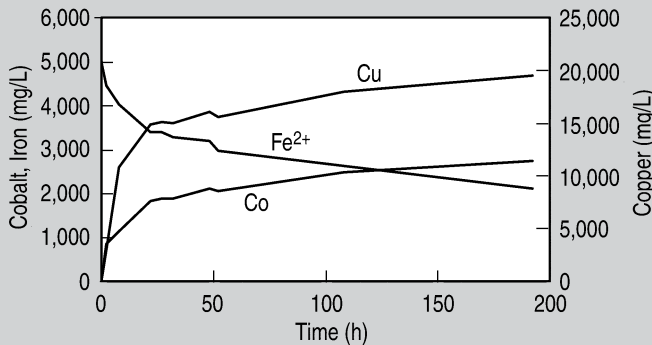


Figure 8. The vat leaching of ore type C (100% minus ¼ inch). Initial: 5 g/L Fe²⁺; temperature: ambient; pH = 1.5.

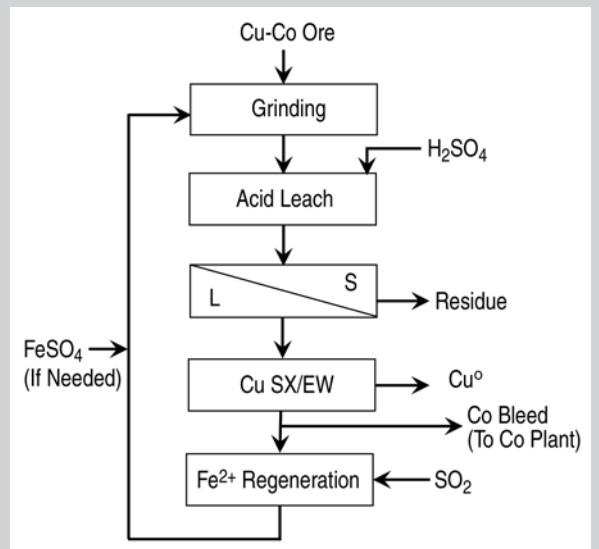


Figure 9. The pilot plant treatment of ore type C (1997).

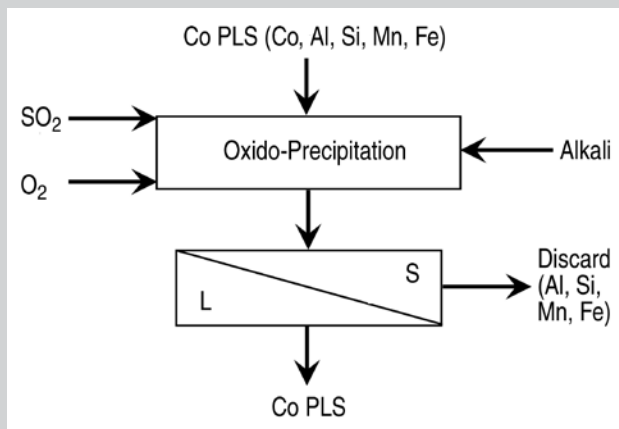


Figure 10. A conceptual process to oxidize/precipitate Fe, Mn during Al, Si hydrolysis using SO₂/O₂ mixtures.

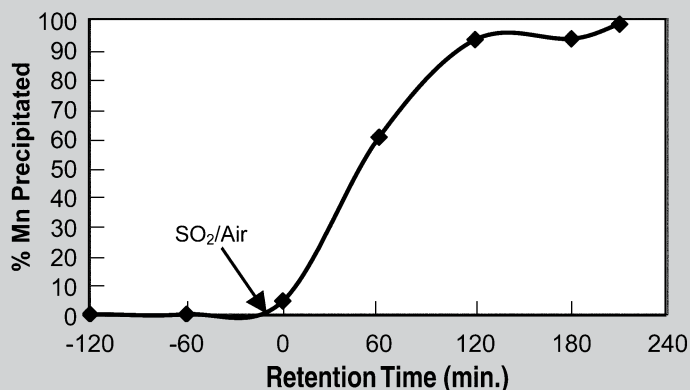


Figure 11. The selective removal of manganese from a cobalt leach solution using SO₂/air mixtures. Temperature: 60°C; 2% SO₂ in air.

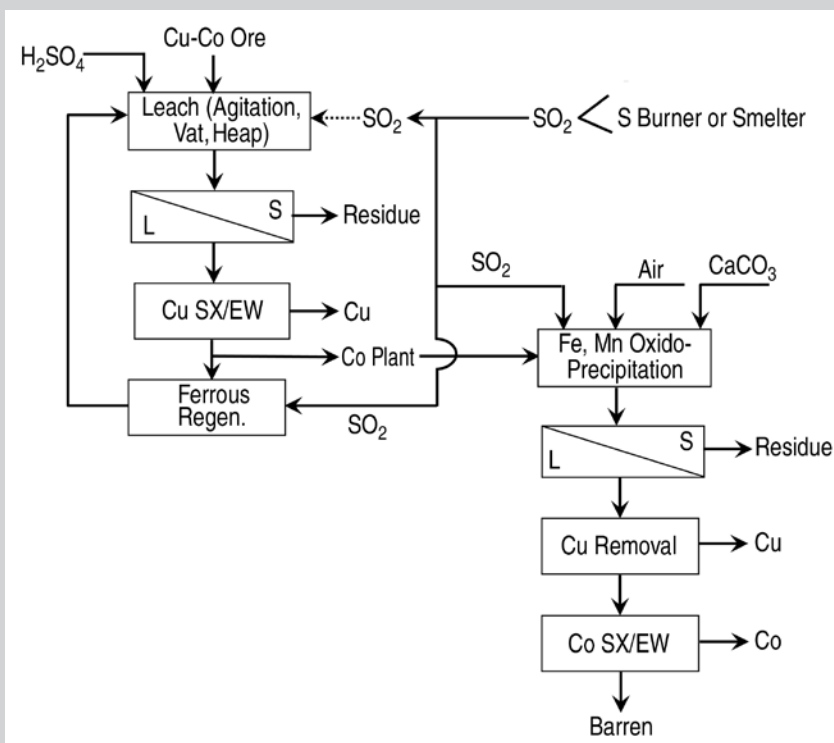


Figure 12. The potential uses of sulfur dioxide during the treatment of cobaltic ores.

containing ferrous sulfate as the primary reductant can be percolated through the vat/heap, and, when needed, ferrous sulfate can be regenerated using SO₂ gas sparged in an agitated reactor. An example of application is presented in Figure 8 for sample C.

In that test, 0.635 cm ore was agglomerated with 2.2 kg H₂SO₄/t of ore, and cured for 24 hours before being placed in a 15 cm column and percolation leached (374 L/h/m²) upflow with a solution containing 30 g/L H₂SO₄ and 5 g/L Fe²⁺. After 8 days, the extraction was 90.4% and 87.4% for copper and cobalt, respectively, and was still continuing, with 2 g/L Fe²⁺ present.

The same concept can easily be applied to an agitated leach process, as illustrated in Figure 9. About 20 tonnes of sample C were pilot tested in 1997 at SGS Lakefield Research using this concept: the ore ground to a P₈₀ of 80 μm was processed through the flow-sheet illustrated in Figure 9 at a flow-rate of 60 kg/h, and leach recoveries of 98.1% copper, 91.8% cobalt were demonstrated.

USE OF SULFUR DIOXIDE MIXTURES TO PURIFY COBALT SOLUTIONS

Reductive leaches of cobaltic ores will also dissolve significant amounts of manganese, as shown earlier. The cobalt leach solution will therefore also contain manganese, iron (from the ferrous sulfate added as reductant), and other impurities (aluminum, silicon, copper, etc.). Such a solution needs to be purified and concentrated (for example, using solvent extraction with Cyanex 272) to produce electrowon cobalt. Typically, hydrolysis to a pH of around 4.5 will eliminate aluminum, silica, and ferric (but not ferrous and manganous ions) without significant cobalt losses. Cobalt-manganese separation from such solutions is not easy but feasible. One method would be to chemically oxidize ferrous and manganous ions prior to hydrolyze them together with aluminum and silica. A simple and fairly inexpensive procedure to oxidize/precipitate manganese from cobalt solutions would be to use SO₂/O₂ mixtures, as per the concept presented in Figure 10.

It has long been known that SO₂/O₂

mixtures, under proper conditions, can act as powerful oxidants for various ions such as iron, cyanide (Inco's process), and manganese,¹⁵ and it can be applied to Co-Mn and Zn-Mn separations. A typical example is presented in Figure 11.

In this application, the leach solution assayed about 7 g/L cobalt and 600 mg/L manganese. That solution was produced during the pilot plant operation described in Figure 9. The results indicated that, as soon as the SO₂/air mixtures were sparged through the cobalt solution (1 vessel volume per minute), the ORP of the pulp rose significantly to >1,200 mV and the manganese precipitated. In less than 2 hours, manganese was reduced to less than 10 mg/L. The process was demonstrated in 1997 at a pilot plant scale (60 L/h of cobalt solution). The manganese precipitate contained less than 0.5% of the cobalt initially present in the leach solution, and the leach solution, after additional purification for copper, was directed to a solvent extraction (Cyanex 272)–electrowinning (SX–EW) circuit, producing good quality cobalt cathodes.

CONCLUSIONS

Despite its negative reputation due to past abuses and deleterious impacts on the environment when not handled properly, sulfur dioxide represents for the metallurgical industries a very useful reagent that is plentiful, effective, and relatively inexpensive. Besides its traditional main use to manufacture sulfuric acid, it could find several applications in the processing of cobaltic ores, as illustrated in Figure 12 for a typical sedimentary copper-cobalt ore.

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