

THE USE OF PEROXYGEN COMPOUNDS IN HYDROMETALLURGY

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1. INTRODUCTION

1.1. Hydrogen Peroxide

In many ways hydrogen peroxide is the ideal reagent in hydrometallurgy. Its decomposition products are only water and oxygen, thus making it pollution free and environmentally acceptable. Although most of its applications make use of its oxidising properties, under appropriate conditions hydrogen peroxide will also behave as a reducing agent, and as a complexing agent. All three types of reaction are used in hydrometallurgy.

(a) As an Oxidant

As an oxidant hydrogen peroxide is suitable for use in both acid and alkaline systems. As a liquid it can be metered directly into reaction vessels.

Comparison of the redox potentials for hydrogen peroxide and other common oxidants show it to be a most powerful oxidant.

In Acid Solution

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad E^\circ = 1.763 \text{v} \]
\[ \text{HClO} + \text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} + \text{Cl}^- \quad E^\circ = 1.482 \text{v} \]
\[ \text{ClO}^- + 3\text{H}^+ + 6\text{e}^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O} \quad E^\circ = 1.451 \text{v} \]
\[ \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \quad E^\circ = 1.224 \text{v} \]

In Alkali

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^- \quad E^\circ = -0.878 \text{v} \]
\[ \text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^- \quad E^\circ = 0.841 \text{v} \]

(b) As a Reductant

In the presence of transition metal compounds in high valency states in acidic solution, hydrogen peroxide behaves as a reducing agent.

Under acid conditions the reduction reaction is considered to be:

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \quad E^\circ = 0.695 \text{v} \]

thus in the reduction of Co (III) to Co (II)

\[ 2\text{Co(OH)}_3 + \text{H}_2\text{O}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{CoSO}_4 + \text{O}_2 + 5\text{H}_2\text{O} \]

As with oxidation, reduction reactions are fast and do not require special pressure vessels and add no foreign ions to the process solution.
(c) As a Complexing Agent
In addition to its oxidation-reduction properties, mention should be made of the ability of hydrogen peroxide to form peroxo-complexes of various transition and actinide metals. Undoubtedly the best known use of this is in the separation of uranium from solutions containing molybdenum and vanadium as impurities. The uranium forms an insoluble peroxide whereas the peroxo-complexes of molybdenum and vanadium are soluble. Other uses have been suggested for the peroxo-complexes in metal separation e.g. in the separation of molybdenum from tungsten-molybdenum solutions (1).

1.2 CARO’S ACID
A limitation on the efficient use of hydrogen peroxide is its tendency to decompose in the presence of some transition metal ions especially at elevated temperatures. This results in the loss of active oxygen. In hydrometallurgy the most convenient way of stabilising the peroxygen content to this type of decomposition is by converting hydrogen peroxide to Caro’s Acid (peroxymonosulfuric acid, H2S05).
This is an even more powerful oxidant than hydrogen peroxide, and at the same time exhibits greater stability in hydrometallurgical solutions. Unlike hydrogen peroxide, it behaves only as an oxidising agent and is therefore capable of completing the more difficult oxidations in acid media. Its $E_o$ value has been deduced by Spiro (2) from published data.

\[
\begin{align*}
\text{HSO}_5^- + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{HSO}_4^- + \text{H}_2\text{O} \\
E_o &= 1.81 \text{V}
\end{align*}
\]

Commercially the preferred route for making Caro’s Acid is by the controlled addition of hydrogen peroxide to concentrated sulphuric acid. Cooling is necessary to remove the heat of reaction and heat of dilution of sulphuric acid:

\[
\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_5 + \text{H}_2\text{O}
\]

This reaction results in an equilibrium mixture of $\text{H}_2\text{SO}_5$ containing some free sulphuric acid and hydrogen peroxide. The composition of the equilibrium mixture is governed by the concentrations and mole ratio of the reactants employed (3). Slow decomposition of the product occurs but this can be almost eliminated by keeping the Caro’s Acid cool before use. It can nonetheless be used in processes occurring at temperatures as high as 90°C as its oxidising reactions are all very much faster than its rate of decomposition.
It should be noted that all of the sulphuric acid going into the preparation is subsequently available to react as sulphuric acid, and so in an acid leach the only extra raw material required to use Caro’s Acid is hydrogen peroxide.
Being both a liquid and highly reactive, process control using Caro’s Acid is often improved. This helps to minimise oxidant consumption and to avoid unreacted oxidant coming in contact with subsequent process steps such as solvent extraction. As with hydrogen peroxide selectivity can be achieved by adjustment of the reaction pH, although the decomposition rate

575
of the Caro's Acid becomes a significant factor above pH 6.0.

Examples of the use of peroxide chemicals in metallurgical extractions and separation are given in the remainder of this paper.

2. LEACHING REACTIONS
2.1 LEACHING OF URANIUM ORES

In conventional acid leaching of uranium ores oxidant is added to ensure that any uranium IV minerals present are oxidised to produce the soluble UO₂⁺ ion. The oxidant acts indirectly by converting iron (II) to iron (III), the iron (III) then oxidises the uranium.

\[
2\text{Fe}^{2+} + 2\text{H}^+ + \text{H}_2\text{O}_2 \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}
\]

\[
\text{UO}_2^+ + 2\text{Fe}^{3+} \rightarrow \text{UO}_2^{2+} + 2\text{Fe}^{2+}
\]

Traditionally pyrolusite or sodium chlorate have been used as oxidants, the choice usually depending upon availability. More recently Caro's Acid has been commercially as an alternative oxidant (4). It is preferred to hydrogen peroxide in such applications due to the inherently much greater stability of Caro's Acid in acid uranium ore slurries especially at elevated temperatures.

Caro's Acid possesses an environmental advantage since its only decomposition products are oxygen, water and sulphuric acid. This is not so with pyrolusite or sodium chlorate. When pyrolusite is used raffinates are produced containing high levels of manganese, a potential heavy metal pollutant. The use of chlorate results in a build up of chloride ions in the mill circuit especially where total water recycle is required. This eventually causes a decrease in solvent extraction efficiency; the high levels of chloride are also objectionable on the grounds that they mobilise radium (5).

The use of Caro's Acid in many instances promotes considerable savings in sulphuric acid consumption during leaching. The acid saved is considerably in excess of that accounted for by the dissolution of pyrolusite. No loss of uranium extraction efficiency is observed:

\[
\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{Mn}^{2+}
\]

\[
\text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}
\]

Examples of acid savings are given in Table 1 from a study of Australian ores (6). The extra acid saving is thought to arise due to reduced gangue dissolution. Where tailings neutralisation is required the lower acid consumption and reduced gangue dissolution constitute a considerable saving in lime. This has been found in practice, the lime saving often exceeding that expected.
Excellent process control can be achieved using Caro’s Acid, since, unlike chlorate and pyrolusite, additions of Caro’s Acid produce an almost instantaneous change in redox potential. This also avoids the use of excessive oxidant, a feature commonly found in mills using pyrolusite where response is usually sluggish.

Hydrogen peroxide finds use in the extraction of uranium from phosphoric acid. The uranium present in phosphoric acid, made from phosphate rock is normally present as both U(IV) and U(VI). Prior to recovery by solvent extraction it is either oxidised completely to U(VI) or all reduced to U(IV) depending upon choice of extractant. In the latter case the uranium is stripped from the organic phase by treatment with an oxidising agent.

2.2 LEACHING OF METAL SULPHIDES

Under acid leaching conditions both H₂O₂ and Caro’s Acid will attack sulphide ores. Elemental sulphur is produced as a by-product (7).

\[
\text{ZnS} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + 2\text{H}_2\text{O} + \text{SO}_2
\]

Using H₂O₂ under alkaline conditions the sulphide is oxidised through to sulphate consequently involving a greater oxidant requirement e.g.

\[
\text{ZnS} + 4\text{H}_2\text{O}_2 \rightarrow 2\text{Zn}^{2+} + \text{SO}_4^{2-} + 4\text{H}_2\text{O}
\]

2.2.1 ZINC SULPHIDE CONCENTRATE

Leaching of zinc sulphide concentrates with hydrogen peroxide at 90°C gave a 99% recovery of zinc. The reaction was carried out in 170 g/l sulphuric acid solution. A redox potential of 500-600 mV was maintained by intermittent peroxide addition. Although some decomposition of the peroxide occurred, only 1.18 times the stoichiometric level of peroxide was required even at the reaction temperature of 90°C. Over 99% of the sulphur was accounted for in elemental form. A similar reaction using Caro’s Acid again gave a 99% recovery of zinc. The total peroxyoxygen addition in this case was only 1.11 times the stoichiometric requirement, indicating the greater stability of Caro’s Acid.

2.2.2 COPPER SULPHIDES AND MIXED OXIDE ORES

The simpler sulphides e.g. covellite (CuS) and chalcocite (Cu₂S), are readily attacked by both hydrogen peroxide and Caro’s Acid to give copper in solution:

\[
\text{CuS} + 2\text{H}_2\text{O}_2 + 4\text{H}^+ \rightarrow 2\text{Cu}^{2+} + 4\text{H}_2\text{O} + \text{SO}_2
\]
\[
\text{Cu}_2\text{S} + 2\text{H}_2\text{SO}_4 + 2\text{H}^+ \rightarrow 2\text{Cu}^{2+} + 2\text{H}_2\text{SO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}
\]
Below pH 2 the reaction stops at the formation of elemental sulphur. As with the zinc sulphide concentrates Caro's Acid is the preferred oxidant. Results are more variable when leaching the complex sulphidic ores such as chalcopyrite. In acid solution the reaction is considered to be:

$$2CuFeS_2 + 5H_2SO_4 + 5H_2O_2 \rightarrow 2CuSO_4 + Fe_2(SO_4)_3 + 4S + 10H_2O$$

Data derived from the leaching of one concentrate gave a 98.7% recovery of the copper after 4 hours leaching at 90°C in sulphuric acid of initial concentration 14 g/l. A second sample however gave a maximum extraction of only 37% yet a detailed mineralogical examination revealed no apparent differences. Individual ores should therefore be examined for suitability. Other sulphide ores that have been examined include pentlandite concentrates and mixed zinc-copper concentrates.

3. OXIDATION REACTIONS IN SOLUTION

Peroxygen chemicals especially Caro's Acid can be used to oxidise metals such as vanadium, chromium and molybdenum rapidly and quantitatively to their highest oxidation states even in acid solution. They may also be used to oxidise iron, especially to remove small amounts and to oxidise and remove arsenic by production of ferric arsenate.

3.1 VANADIUM

Vanadium often occurs in uranium ores and is recovered as a by-product in the extraction of uranium if present in sufficient amounts. After leaching of the ore, both uranium and vanadium are present in solution in the U (VI) and V(IV) oxidation states respectively. After removal of the uranium by solvent extraction the vanadium is then recovered by oxidation to the V(V) state followed by solvent extraction.

The oxidation potential for vanadium (IV) in acid solution is high.

$$VO_2^++H_2SO_5 + e^- \rightarrow VO_2^+ + H_2SO_4 \quad E_0 = 1V$$

Thus for oxidation to proceed strong oxidants are required. Both chlorate and hydrogen peroxide have been used commercially, however both suffer from disadvantages. Chlorate oxidation is slow except at high acidity and also contaminates the system with chloride ions. Being slow to react the reaction becomes difficult to control, and any excess of chlorate is absorbed onto the extractant, lowering its capacity and promoting oxidative degradation. Hydrogen peroxide will oxidise vanadium from V(IV) to V(V) which immediately combines with the hydrogen peroxide to form a red peroxo-vanadium (V) complex. However subsequent decomposition of the complex yields both VO$_2^+$ ions in solution and VO$_2^+$ as a result of a reduction side reaction.

To maximise vanadium (V) formation an excess of peroxide is required of up to five times the stoichiometric level.
In contrast Caro's Acid results in a stoichiometric conversion to V(V). Caro's Acid of low residual hydrogen peroxide content should be used to avoid any reduction occurring. The reaction can be carried out over a wide range of pH and temperature, and, being stoichiometric avoids any excess of oxidant attacking the extraction medium.

The work has been successfully transferred to commercial liquors derived from the leaching of a carnottite ore (8).

3.2 CHROMIUM

In acid solution chromium is oxidised from chromium (III) to chromium (VI) by the use of Caro's Acid. In alkaline solutions hydrogen peroxide may be used.

3.3 MOLYBDENUM

In the leaching of uranium/molybdenum bearing ores the molybdenum is leached out in both the Mo (V) and Mo (VI) oxidation states. In order to remove all of the uranium and molybdenum by solvent extraction it is necessary to convert all of the molybdenum to its highest oxidation state.

Oxidation to the Mo (VI) state is essential since any molybdenum remaining as Mo (V) leads to third phase formation and hence poor extraction. In Brazilian ores examined, the ratio of Mo (VI) / Mo (V) in the leach solution is usually about 4:1. Although normally considered as sensitive to air oxidation Mo (V) enjoys a surprising stability in the acid lixiviant, and an oxidant is usually required to ensure full conversion.

Chlorate may be used, but as with vanadium, unless at low pH or elevated temperatures reaction is very slow and difficult to control resulting in unreacted oxidant finding its way into the solvent extraction circuit. Both hydrogen peroxide and Caro's acid are capable of oxidising Mo (V) to Mo (VI), the reaction can be carried out at ambient temperatures and over a wide range of pH values. Reactions are fast and stoichiometric with respect to the molybdenum content, being complete in 10-30 minutes compared to 6-17 hours associated with chlorate:

\[ 2\text{Mo}^5+ + 2\text{H}^+ + \text{H}_2\text{O}_2 \rightarrow 2\text{Mo}^6+ + 2\text{H}_2\text{O} \]

The system is also free of chloride ions, thus minimising effluent disposal and allowing total water recycle where necessary.

4. OXIDATIVE HYDROLYSES

In acid solution Caro's Acid is sufficiently powerful to oxidise manganese (II) to manganese (IV), the latter precipitating as the oxide MnO₂. Manganese containing solutions may be oxidised directly but the reaction is catalysed by certain transition metal ions. The reaction proceeds according to the equation:

\[ \text{Mn}^{2+} + \text{H}_2\text{SO}_5 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + \text{H}_2\text{SO}_4 + 4\text{H}^+ \]

Caro's Acid must be used under acid conditions since hydrogen peroxide acts as a reducing agent for MnO₂:

\[ \text{MnO}_2 + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \]

Use has been made of this reaction in relation to the demanganising of zinc electrolyte solutions and cobalt/nickel solutions prior to cobalt removal.
6. HYDROGEN PEROXIDE AS REDUCING AGENT
Hydrogen peroxide unlike Caro's Acid may under certain circumstances act as a reducing agent and this has been referred to previously in the text. Use can be made of this fact however since peroxide will react rapidly and cleanly as reducing agent much the same as it does as an oxidant.

The reduction reaction may be considered as:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E_0 = 0.695V$$

Thus hydrogen peroxide is theoretically capable of reducing metals in high oxidation states such as Co (III), V (V), Cr (VI) and Mn (IV).

Hydrogen peroxide is used commercially to generate divalent cobalt from cobaltic hydroxide under acid conditions:

$$2Co(OH)_3 + H_2O_2 + 2H_2SO_4 \rightarrow 2CoSO_4 + O_2 + 6H_2O$$

The reaction which occurs rapidly and quantitatively according to the stoichiometric equation has the advantage of working in dilute acid and at ambient temperature. It also avoids the need for formalin solution or storage of methanol.

7. AVAILABILITY OF HYDROGEN PEROXIDE AND CARO'S ACID FOR HYDROMETALLURGY
Hydrogen peroxide is produced on a large scale in many countries, and total production worldwide is estimated to be about 500,000 tons per annum. An important plant is located in Brazil at Elector in Sao Paulo state. This plant is operated by Peroxidos do Brasil - part of the worldwide interox group of companies. Hydrogen peroxide is readily transported in bulk and so can be delivered to mines in remote locations and to countries without their own production facilities. Under normal conditions of transport and storage ordinary commercial grades of hydrogen peroxide lose only 1-2% of their active oxygen content per year. Provision for this light loss is made by venting all transport and storage vessels. Caro's Acid is normally made at the user's site. Further details about the handling and use of both products can be given by me or by my colleagues from Peroxidos do Brasil during and after this conference.
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REFERENCES