

# Copper Chemistry

## History

For the chapter on Copper chemistry from the Elsevier text "Chemistry of the Elements" by Greenwood and Earnshaw see [On-Line Metals Based Surveys](#) (This site now seems to have gone off-line).

The [Copper Development Association, Inc](#) (on their Copper Page) makes the point that:

" For nearly 5000 years copper was the only metal known to man. Today it is one of the most used and reused of our modern metals."

Humans first used copper about 10,000 years ago. A copper pendant discovered in Northern Iraq is thought to date back to around 8700 BC. Prehistoric man probably used copper for weapon making. Ancient Egyptians too seemed to have appreciated the corrosion resistance of the metal. They used copper bands and nails in ship building and copper pipes were used to convey water. Some of these artifacts survive today in good condition. An estimate of the total Egyptian copper output over 1500 years is 10,000 tons.



Years later, copper alloys appeared. Bronzes (copper-tin alloys) came about first followed much later by brass (copper-zinc alloys). The " Bronze Age" saw the extensive use of copper and bronze for arms, coins, household utensils, furniture and other items. The earliest known example of brass use is a Roman coin minted during the reign of Augustus 27 BC- AD 14. Copper later played an important role in the advent of electricity and today is still among our most valued materials.

Usage of copper compounds also dates back to before 4000 BC. Copper sulphate for example was an especially important compound in early times. Ancient Egyptians used it as a mordant in their dyeing process. The compound was also used to make ointments and other such preparations. Later, medicinal use of copper sulphate came about with its prescription for pulmonary diseases. Copper sulphate is still extensively used today and no harmful side effects of its *prescribed* use have been reported.

## Occurrence

Copper is the earth's 25<sup>th</sup> most abundant element, but one of the less common first row transition metals. It occurs as a soft reddish metal that can be found native as large boulders weighing several hundred tons or as sulphide ores. The latter are complex copper, iron and sulphur mixtures in combination with other metals such as arsenic, zinc and silver. The copper concentration in such ores is typically between 0.5-2%.

The commonest ore is chalcopyrite,  $\text{CuFeS}_2$ , a brass yellow ore that accounts for approximately 50% of the world's copper deposits. Numerous other copper ores of varying colours and compositions exist. Examples are malachite,  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ , a bright green ore, and the red ore cuprite,  $\text{Cu}_2\text{O}$ .

Copper occurs in biological systems as a part of the prosthetic group of certain proteins. For examples of copper containing proteins see the article at the [University of Leeds, Department of Biochemistry and Molecular Biology](#).

The red pigment in the [softbilled Touraco Bird](#) contains a copper porphyrin complex. The pigment is highly water soluble under alkaline conditions so fortunately the bird lives in tropical rain forests!

### Properties of copper

An excellent site for finding the properties of the elements, including copper is at



Another useful link is to the [Geology Project pages](#) at the Univ. of Nevada, Reno.

### The Extraction of Copper

Copper is extracted from its ore by two principal methods:

1. Pyrometallurgical method
2. Hydrometallurgical method

#### Pyrometallurgical Method

This technique is often used in the extraction of sulphide ores. There are four main stages:

- Mining and Milling  
The ore is crushed and ground into a powder usually containing less than 1% copper. Minerals are concentrated into a slurry that is about 15% copper. Copper minerals are separated from useless material by flotation using froth forming solutions.
- Smelting  
Smelting of the copper concentrate and extraction by heat, flux and addition of oxygen. Sulphur, iron and other undesirable elements are removed and the product is called blister copper.
- Refining  
This is the final stage in the process for obtaining high grade copper. Fire and electro-refining methods are the techniques used. The latter produces high purity copper fit for electrical uses.

#### Hydrometallurgical Method -SX/EW

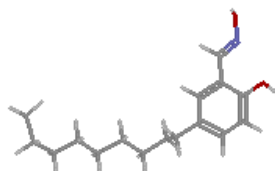
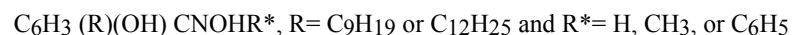
Solvent Extraction / Electrowinning is the most dominant leaching process used today in the recovery of copper from chemical solutions. As the name suggests the method involves two major stages:

Solvent Extraction- the process by which copper ions are leached or otherwise extracted from the raw ore using chemical agents.

Electrowinning- electrolysis of a metal ion containing solution such that Cu ions within it are plated onto the cathode and thereafter removed in elemental form.

The process takes place in the following steps:

- A lixiviant (leaching solution) is selected for use in leaching Cu ions from the ore. Common reagents are weak acids e.g.  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ , acidic chloride solutions e.g.  $\text{FeCl}_2$ , ammonium chloride and ammonium salt compositions.
- When applied to the ore the chosen lixiviant dissolves the copper ions present to give a lixiviant product called a "pregnant leach solution".
- An organic extractant is then selected to remove Cu ions from the aqueous solution. Preferred organic extractants consist of hydroxyphenyl oximes having the basic chemical formula:



Examples of such extractants are 5-nonylsalicylaldoxime and a mixture of this compound and 2-hydroxy-5-nonyl-acetophenone oxime. The commercially available reagents usually contain 5%-10% of the oxime in a 90-95% petroleum dilutant such as kerosene.

Prior to mixing with lixiviant product the extractant will contain little or no copper and is at this stage called the "barren organic extractant".

- Copper ions are transferred from the leaching solution to the organic extractant upon mixing of the two reagents. A phase separation takes place to give an aqueous and an organic phase termed the first aqueous and first organic phases respectively. The first aqueous phase, the "raffinate", is the lixiviant stripped of its copper ions while the first organic phase is the "loaded organic extractant" i.e. extractant with copper ions present.
- The raffinate is recycled to the leaching pad while the loaded organic extractant is mixed with an electrolyte solution called the "lean electrolyte" (i.e. containing no copper). Typical electrolytes are acidic solutions such as sulphuric acid,  $\text{H}_2\text{SO}_4$ . The copper ions that were present in the organic extractant thus dissolve in the electrolyte solution to give a copper containing "rich electrolyte." Here again there is a phase separation. The second organic phase is the barren organic extractant while the second aqueous phase is the "rich electrolyte". The barren organic extractant is then recycled for reuse in application to lixiviant product.
- The final stage of the process is the electrolysis of the acidic metal ion solution. As a result dissolved copper ions become plated onto the cathode and elemental copper is removed. The recovery process is thus complete.

### A Note on Impurities

The presence of suspended contaminants within a SX/EW system can significantly compromise its operating efficiency. Such contaminants may be introduced into the system from the ore or from the surroundings. The system is susceptible to contamination from rain, wind and other environmental forces since the first containment vessel, which stores lixiviant product, is typically uncovered and located outdoors. Thus solid waste material in the form of dirt, sand, rock dust, vegetable matter, mineral residue and suspended solids is often introduced into the system in the early stages and persists in the subsequent stages of the process.

The effects of these contaminants are considerable and include:

- increased phase separation time at stages when organic and aqueous solvents are mixed.
- lack of complete phase separation after extraction, this results in loss of expensive organic extractant since much of it remains within the aqueous solution.
- a decrease in the current efficiency and reduction in the purity of the plated copper product in the electrolysis stage.

In most SX/EW systems purification steps have been introduced in order to alleviate this problem. In [US patent \(number 573341\)](#) for example, at least a portion of the second organic phase is filtered to remove solid contaminants before reuse in treating lixiviant product. The recycled organic extractant therefore contains little or no impurities dependent on whether a portion or the entire second organic phase was filtered. It has been found that this filtration step considerably improves the operating efficiency, even when only a portion of the extractant is treated.

### Uses of copper and its compounds

Copper is second only to iron in its usefulness down the ages. The metal and its compounds are used in every sphere of life from the electrical to medicinal and agricultural industries.

#### Uses of copper metal

The electrical industry is the beneficiary of most of the world's copper output. The metal is used in the manufacture of electrical apparatus such as cathodes and wires.

Other uses include:

- Roofing
- Utensils
- Coins
- Metal work
- Plumbing
- Refrigerator and Air Conditioning coils
- Alloys e.g. bronze, brass

#### Uses of copper compounds

Copper compounds have their most extensive use in Agriculture. Since the discovery of their toxicity to certain insects, fungi and algae these compounds have been used in insecticides, fungicides and to prevent algal development in potable water reservoirs. They are therefore used in the control of animal and plant diseases. Fertilisers are also often supplemented with copper compounds, e.g. copper sulphate, in order to increase soil fertility and thus boost crop growth.

Copper compounds are also used in photography and as colourants for glass and porcelain.

## Copper for Good Health

Copper is one of many trace elements required for good health. It is part of the prosthetic groups of many proteins and enzymes and thus is essential to their proper function. Since the body can not synthesize copper it must be taken in the diet. Nuts, seeds, cereals, meat (e.g. liver) and fish are good sources of copper.

Copper has also found medicinal use. It has been used from early times in the treatment of chest wounds and water purification. It has recently been suggested that copper helps to prevent inflammation associated with arthritis and such diseases. Research continues into medicines containing copper for treatment of this and other conditions.

For more information on the importance of copper to health and copper deficiency see: [MotherNature](#) and/or [Vitamin Research Products](#)

## Copper Compounds

Copper exhibits a variety of compounds, many of which are coloured. The two principal oxidation states of copper are +1 and +2 although some +3 complexes are known. Copper(I) compounds are expected to be diamagnetic in nature and are usually colourless, except where colour results from charge transfer or from the anion. The +1 ion has tetrahedral or square planar geometry. In solid compounds, copper(I) is often the more stable state at moderate temperatures.

The copper(II) ion is usually the more stable state in aqueous solutions. Compounds of this ion, often called cupric compounds, are usually coloured. They are affected by [Jahn Teller distortions](#) and exhibit a wide range of stereochemistries with four, five, and six coordination compounds predominating. The +2 ion often shows distorted tetrahedral geometry.

## Copper Halides

All of the copper(I) halides are known to exist although the fluoride has not yet been obtained in the pure state. The cuprous chlorides, bromides and iodides are colourless, diamagnetic compounds. They crystallize at ordinary temperatures with the zinc blende structure in which Cu atoms are tetrahedrally bonded to four halogens. The copper(I) chloride and bromide salts are produced by boiling an acidic solution of copper(II) ions in an excess of copper. On dilution, the white CuCl or the pale yellow CuBr is produced. Addition of soluble iodide to an aqueous solution of copper(II) ions results in the formation of a copper(I) iodide precipitate, which rapidly decomposes to Cu(I) and iodine.

The copper(I) halides are sparingly soluble in water and much of the copper in aqueous solution is in the Cu(II) state. Even so, the poor solubility of the copper(I) compounds is increased upon addition of halide ions. The table below shows some properties of copper(I) halides.

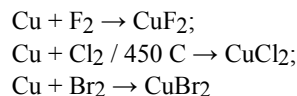
Copper(II) halides

Formula	Colour	MP	BP	m (BM)	Structure
CuF <sub>2</sub>	white	950decomp	-	1.5	
CuCl <sub>2</sub>	brown	632	993decomp	1.75	<a href="#">CuCl<sub>2</sub></a>
CuBr <sub>2</sub>	black	498	-	1.3	

All four copper(II) halides are known although cupric iodide rapidly decomposes to cuprous iodide and iodine. The yellow copper(II) chloride and the almost black copper(II) bromide are the common halides. These compounds adopt a structure with infinite parallel bands of square CuX<sub>4</sub> units. Cupric chlorides and bromides are readily soluble in water and in donor solvents such as acetone, alcohol and pyridine.

Copper(II) halides are moderate oxidising agents due to the Cu(I)/ Cu(II) couple. In water, where the potential is largely that of the aqua-complexes, there is not a great deal of difference between them, but in non-aqueous media, the oxidising (halogenating) power increases in the sequence; CuF<sub>2</sub> << CuCl<sub>2</sub> << CuBr<sub>2</sub>.

They can be prepared by direct reaction with the respective halogens:



Alternatively they can be prepared from  $\text{CuX}_2 \cdot \text{aq}$  by heating  $\rightarrow \text{CuX}_2$

#### Copper(I) halides

Formula	Colour	MP	BP	Structure
CuCl	white	430	1359	-
CuBr	white	483	1345	-
CuI	white	588	1293	<a href="#">Zinc Blende</a>

Prepared by reduction of  $\text{CuX}_2 \rightarrow \text{CuX}$ ;

except for the F which has not been obtained pure.

Note that  $\text{CuI}_2$  has not been isolated because of the ease of reduction to CuI.

#### Copper Oxides

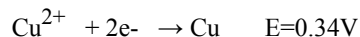
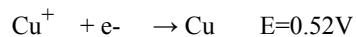
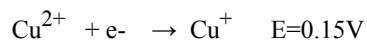
Copper(I) oxides are more stable than the copper(II) oxides at high temperatures. Copper(I) oxide occurs native as the red cuprite. In the laboratory, the reduction of [Fehling's solution](#) with a reducing sugar such as glucose produces a red precipitate. The test is sensitive enough for even 1 mg of sugar to produce the characteristic red colour of the compound. Cuprous oxide can also be prepared as a yellow powder by controlled reduction of an alkaline copper(II) salt with hydrazine. Thermal decomposition of copper(II) oxide also gives copper(I) oxide since the latter has greater thermal stability. The same method can be used to prepare the compound from the copper(II) nitrate, carbonate and hydroxide.

Copper(II) oxide occurs naturally as tenorite. This black crystalline solid can be obtained by the pyrolysis of the nitrate, hydroxide or carbonate salts. It is also formed when powdered copper is heated in air or oxygen. The table below shows some characteristics of copper oxides.

#### Copper oxides

Formula	Colour	Oxidation State	MP
CuO	black	$\text{Cu}^{2+}$	1026decomp
$\text{Cu}_2\text{O}$	red	$\text{Cu}^+$	1230

#### Redox Chemistry of Copper



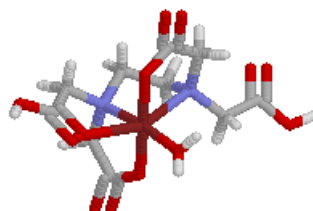
By consideration of this data, it will be seen that any oxidant strong enough to convert Cu to  $\text{Cu}^+$  is more than strong enough to convert  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  (0.52 cf. 0.14V). It is not expected therefore that any stable  $\text{Cu}^+$  salts will exist in aqueous solution.

Disproportionation can also occur:



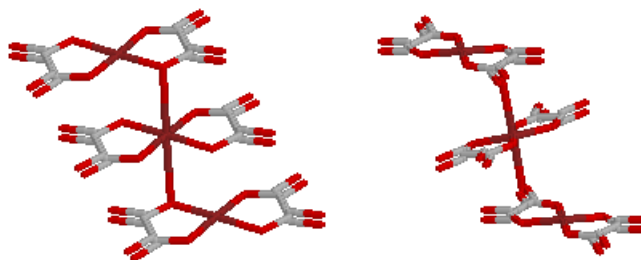
### Coordination complexes

The reaction of EDTA<sup>4-</sup> with copper(II) gave a complex where the EDTA was found to be pentadentate NOT hexadentate, unlike other M(II) ions.



$\text{Cu}(\text{EDTA})^{2-}$

The structure of the  $[\text{Cu}(\text{ox})_2]^{2-}$  ion can be described as square planar or as a distorted octahedron when the packing in the crystal lattice is considered. In the case of the sodium salt, the individual units are parallel in the cell with the copper linked to the oxygens coordinated to the copper in the units sitting both above and below, whereas in the potassium salt, the units are not parallel and when looking at three units the central one is almost at right angles to the other two. Here the copper is linked to one of the non-coordinated oxygens in the units above and below it.



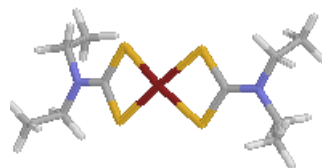
$\text{Na}^+$  and  $\text{K}^+$  salts of  $[\text{Cu}(\text{ox})_2]^{2-}$

$\text{Cu}(\text{OH})_2$  reacts with  $\text{NH}_3$  to give a solution which will dissolve cellulose. This is exploited in the industrial preparation of Rayon. The solutions contain tetrammines and pentammines. With pyridine, only tetrammines are formed eg  $\text{Cu}(\text{py})_4\text{SO}_4$ .

The reaction of copper(II) with amino-acids has been extensively studied. In nearly all cases the product contains the groups in a *trans* configuration, which is expected to be the more stable. In the case of glycine, the first product precipitated is always the *cis*- isomer which converts to the *trans*- on heating. See the [Laboratory Manual for C31L](#) for more details.

### Analytical Determination of Copper(II)

A useful reagent for the analytical determination of the copper(II) ion is the sodium salt of N,N-diethyldithiocarbamate. In dilute alcohol solutions the presence of trace levels of  $\text{Cu}^{2+}$  is indicated by a yellow colour, which can be measured by a spectrophotometer, and the concentration determined from a Beer's Law plot. The complex is  $\text{Cu}(\text{E}^{\text{d}}\text{d}^{\text{c}})_2$ , which can be isolated as a brown solid.

 $\text{Cu}(\text{Et}_2\text{dtc})_2$ **References:**

- "Complexes and First-Row Transition Elements", D. Nicholls  
"Basic Inorganic Chemistry", F.A. Cotton, G. Wilkinson and P.L. Gaus  
"Advanced Inorganic Chemistry", F.A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann  
"Chemistry of the Elements", Greenwood and Earnshaw

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