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THE HISTORY OF COPPER CEMENTATION ON IRON – THE WORLD'S FIRST HYDROMETALLURGICAL PROCESS FROM MEDIEVAL CHINA*

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ABSTRACT

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'Cementation' is an important unit process in hydrometallurgical engineering and is used to precipitate a metal from its solution onto another metal that is more electropositive. The precipitation of copper on iron from natural solution is a classical example of a relatively ancient art which has been applied successfully for centuries to produce copper on a commercial scale. The method applied to extraction of copper from mine water has been practiced in China since 1086 A.D., in the Northern Sung period (960—1126 A.D.). This occurrence is many centuries earlier than any in Europe and other places of the world. The early development of the process is thought to be a contribution by medieval Chinese alchemists. The results of a study on the historical development of copper cementation in China are presented in this paper.

INTRODUCTION

'Cementation' is the term used in hydrometallurgy to describe the electrochemical precipitation of a metal from a solution of its salts onto a more electropositive metal. In general, the precipitation or cementation reaction can be expressed as:

$$n\,M^{m+} + m\,N \rightarrow n\,M + m\,N^{n+}$$

The most common industrial cementation operations include the use of zinc dust to precipitate gold and silver from cyanide solutions, and the use of iron to recover copper from copper-bearing solutions. The precipitation of copper on iron from its salt solutions employs one of the earliest known chemical processes, specifically:

$$\underset{(aq)}{CuSO_4} + \underset{(s)}{Fe} \rightarrow \underset{(s)}{Cu\downarrow} + \underset{(aq)}{FeSO_4}$$

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a process that is more commonly referred to as cementation. Over many centuries the high commercial value of this process has been proved in the majority of the world's copper districts. Even today, copper cementation with scrap iron is still used in commercial operations by some mines, although it has been superceded by the solvent extraction–electrowinning process. In China, the earliest recorded date of commercial operations for the production of cement copper is 1086 A.D. in the Northern Sung period [1]. This is several centuries earlier than first recorded date in Europe. The production of cement copper in a peak year in the reign of Shao–Hsing (1131–1162 A.D.) of the Sung dynasty reached 1,874,428 catties (equivalent to 1,124,657 kg) [2]. Between the 11th and the 12th centuries, copper produced from copper-bearing mine waters and vitriolic earthy matter by cementation was one of the major sources of the copper used for coinage in China. The recognition of the reaction that cupric ions in water or acetic solution can be replaced by iron is believed to have been contributed mainly by Chinese alchemists of the Han dynasty (206 B.C.–220 A.D.). Some important aspects of the history of development of copper cementation are described in this paper.

HISTORICAL BACKGROUND

The recovery of copper by precipitation from its aqueous solutions using iron has been utilized in China since 1086 A.D. However, as recorded in various books written in the years between the 2nd century B.C. and the 2nd century A.D., a reaction was noted to occur when green or blue copper minerals were physically in contact with an iron object, the surface of which could thus become coppery. A paragraph in *Huai-nan Wan Pi Shu* (The Ten Thousand Infallible Arts of the Prince of Huai-Nan) [3], a book of the 2nd century B.C., says:

> When *pei ching*[a]* (a pale-green mineral) is in contact with iron, the iron immediately turns into copper.

Another book, *Shen-Nung Pên-Tschao Ching* (Classical Pharmacopoeia of the Heavenly Husbandman) [4], compiled before the 2nd century and based on earlier material, also gives the same citation:

> *Shih tan*[b] (a copper sulfate mineral) can turn iron into copper.

The first recipe of the *San-shih-liu Shui Fa* (Thirty-six Methods of Making Mineral Solutions) [5], a book describing the making of aqueous solutions from mineral substances in ancient times, describes the method of making *fan-shih shui*[c] (aqueous solution of *fan shih*[d]) as follows:

> Take 1 catty of *fan shih*[d] (a copper-bearing iron sulfate mineral) in the shape of a 'horse-tooth' and without 'gall'; place it in a green-bamboo tube which has a shaved thin wall. Use 0.25 catty of nitre to cover the top and bottom of the tube and seal

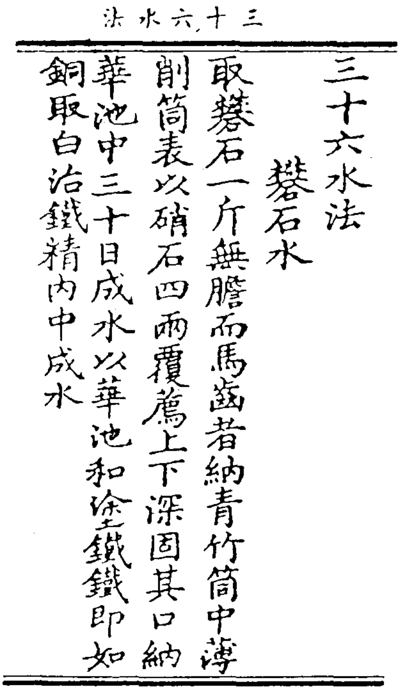
*See Explanatory Notes.

the openings tightly. Immerse it in *hua chhih*[e] (vinegar pool) for 30 days, then an aqueous solution is formed. After mixing with vinegar and smearing the solution on iron, the iron will show a reddish color resembling copper. Iron dust dropped into the solution will be dissolved.

The recipe is the earliest in the literature describing precipitation of copper on iron from its solution (Fig. 1). The book is probably a work originating in the Eastern Han period (25—220 A.D.), and the recipe must have been used for alchemical preparations. It is quite clear that, in all the above-referenced literature, any iron object will turn into copper after being reacted with some copper minerals or solutions. Later, in the 6th century, Thao Hung-Ching, a great Taoist and physician, wrote the following paragraph in his book of *Pên-Tshao Chi Chu* (Collected Commentaries on the Classical Pharmacopoeia of the Heavenly Husbandman) [6]:

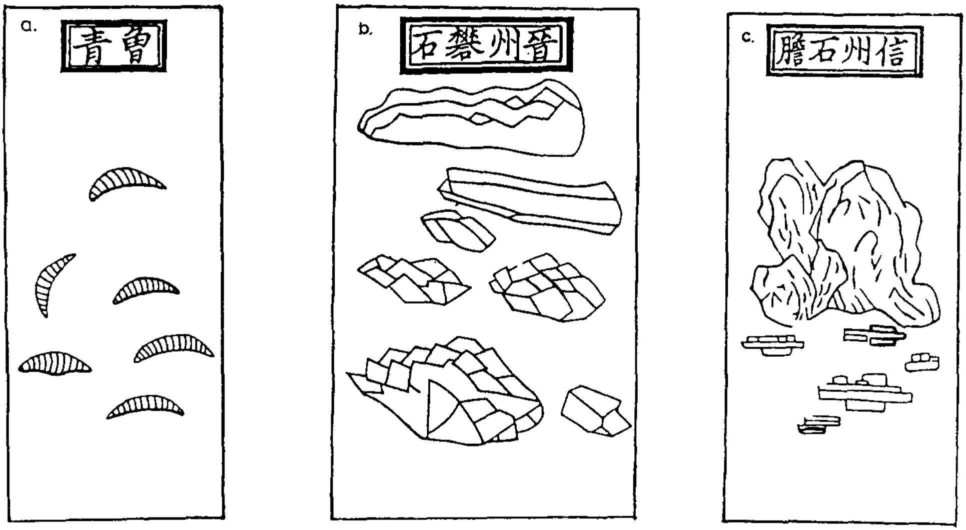
The dark yellow sorts (of alum) are called '*shi-shih fan*'[f] (a copper mineral); these are not used in pharmacy but are only suitable for the plating of metal. Mix first with refined copper, then drop it into vinegar. The solution is used to smear the surface of iron; the iron is turned to the colour of copper. Although the outside colour becomes copperish, the material inside remains quite unchanged.

Since colour is the primary basis for mineral nomenclature and classification in ancient times of any civilization, confusion may arise in the application of


三十六水法

三十六水法
礬石水
取礬石一斤無膽而馬齒者納青竹筒中薄
削筒表以硝石四兩覆薦上下深固其口納
華池中三十日成水以華池和塗鐵鐵即如
銅取白治鐵精內中成水

Fig. 1. The earliest recipe describing the method of precipitating copper on iron from its solution, from *San-shih-liu Shui Fa* (Thirty-six Methods of Making Mineral Solutions) author and date unknown, probably a work of the Eastern Han period (25—220 A.D. [5].



a. *tsheng chhing* (曾青) azurite.

b. Chin-chou *fan shih* (晉州礬石), a copper-bearing sulphate mineral from Chin-chou.

c. Hsin-chou *shih tan*. (信州石膽), chalcanthite from Hsin-chou.

Fig. 2. Illustrations of some easily soluble copper minerals in medieval China, from *Ching Shih Cheng Lei Ta-Kuan Pên-Tshao* (The Classified and Consolidated Pharmacopoeia of the Ta-Kuan Reign), first print 1108 [7].

these names. There are many reasons to believe that the above-mentioned minerals come under the category of copper sulfate or carbonate in different varieties. The illustrations of some water- or acetic acid-soluble copper minerals are reproduced in Fig. 2 with rearrangement from *Ching Shih Cheng Lei Ta-Kuan Pên-Tshao* (The Classified and Consolidated Pharmacopoeia of the Ta-Kuan Reign) [7], a book written at the dawn of the 12th century.

From the above literature, we can reach the conclusion that the ancient Chinese alchemists, through their alchemical practices, recognized the reaction of copper precipitation from its solution on iron before the end of Eastern Han period (220 A.D.). Nevertheless, it still took several centuries to develop this reaction into a commercial process for production of cement copper.

ORIGIN OF COPPER CEMENTATION IN CHINA

After the founding of the Sung dynasty (960 A.D.) in China, the unified kingdom significantly increased its agricultural and industrial production in almost every aspect. At the time, the main currency consisted of copper coins. For taxation, trading, and other purposes, the use of coins needed for circulation reached a level that had never been experienced before. The increasing demand for copper for coin minting and for other uses gave the government an opportunity to try new methods for obtaining extra copper from solution to compensate for the diminishing supply of smelted copper from ores. However, in the 10th century, the method of transmuting iron to copper was still a secret technique known to Taoists or alchemists.

In the last quarter of the 11th century, there was evidence that the process had been suggested for production testing. In Su Chhe's book *Lung-chhuan Lueh Chih* (Brief Jottings of Dragon-Stream) [8], the author tells us an interesting story regarding this scepticism about the process. The story 'Disbelief of the secret method that can convert iron into copper' can briefly be rendered as follows:

> There was a merchant who reported to the government treasurer that he knew of a secret method for using *tan fan*[g] (gall vitriol) to convert iron into copper. I asked him to come before me and I told the merchant that the secret methods were forbidden. I also told him that, if he knew it, it must be a real process. Since the method had to be tested officially, it had to be disclosed to the public and it would then be no longer a secret.... As a state administrator, I was not allowed to do things against the national law. The merchant left regretfully. I reported this matter to the Capital immediately. My colleagues doubted the story, and ordered to have the method tested with a horse-cutting knife, and it failed.

This was about the year 1080 A.D. The reason for the failure of the test was that the reaction taking place between a copper sulfate mineral and an iron article in physical contact is very slow and not easily noticed. The reaction takes place much faster by employing an aqueous solution of *tan fan*[g] (chalcanthite, $CuSO_4 \cdot 5H_2O$) instead of the mineral itself. Undoubtedly, this must have been the merchant's secret not mentioned to the officials.

Since that time, two stories dating from the Sung dynasty (960—1279 A.D.) show real observations of the precipitation of metallic copper on iron from its aqueous solutions. The first one was recorded by the great scientific scholar Shen Kua (1030—1094 A.D.) in his book *Meng-Chhi Pi Than* (Dream-Pool Essays) [9], which was written in 1086 A.D. The passage goes as follows:

> In the Chhien-shan district of Hsin-chou, there is a bitter spring which forms a rivulet at the bottom of a gorge. When its water is heated it becomes *tan fan*[g]. When *tan fan* is heated it gives copper. If this 'alum' is heated for a long time in an iron pan the pan is changed to copper. Thus water can be converted into copper — an extraordinary change of substance, really unimaginable.

The second story was given by Chou Hui in 1192 A.D. in his book entitled *Ching-Po Tsa Chih* (Memoirs of Green-Wave) [10]. The story is:

> In the Chhien-shan district of Hsin-chou, there used to be a stream of (blue) vitriol water (*tan shui*)[h] flowing down out of the mountains over some waterfalls. It was utilised in the 'steeping method' (*chhin thung*)[d] of making copper for the melters. The flow continued even when the climate was dry, more abundantly in spring and summer, less so in autumn and winter. It is said that in olden times a man lost his keys in the water and when he recovered them on the following day, they had all turned to copper. In recent years the stream had almost stopped flowing, so the 'steeping method' took longer and required more labour. Formerly there were some

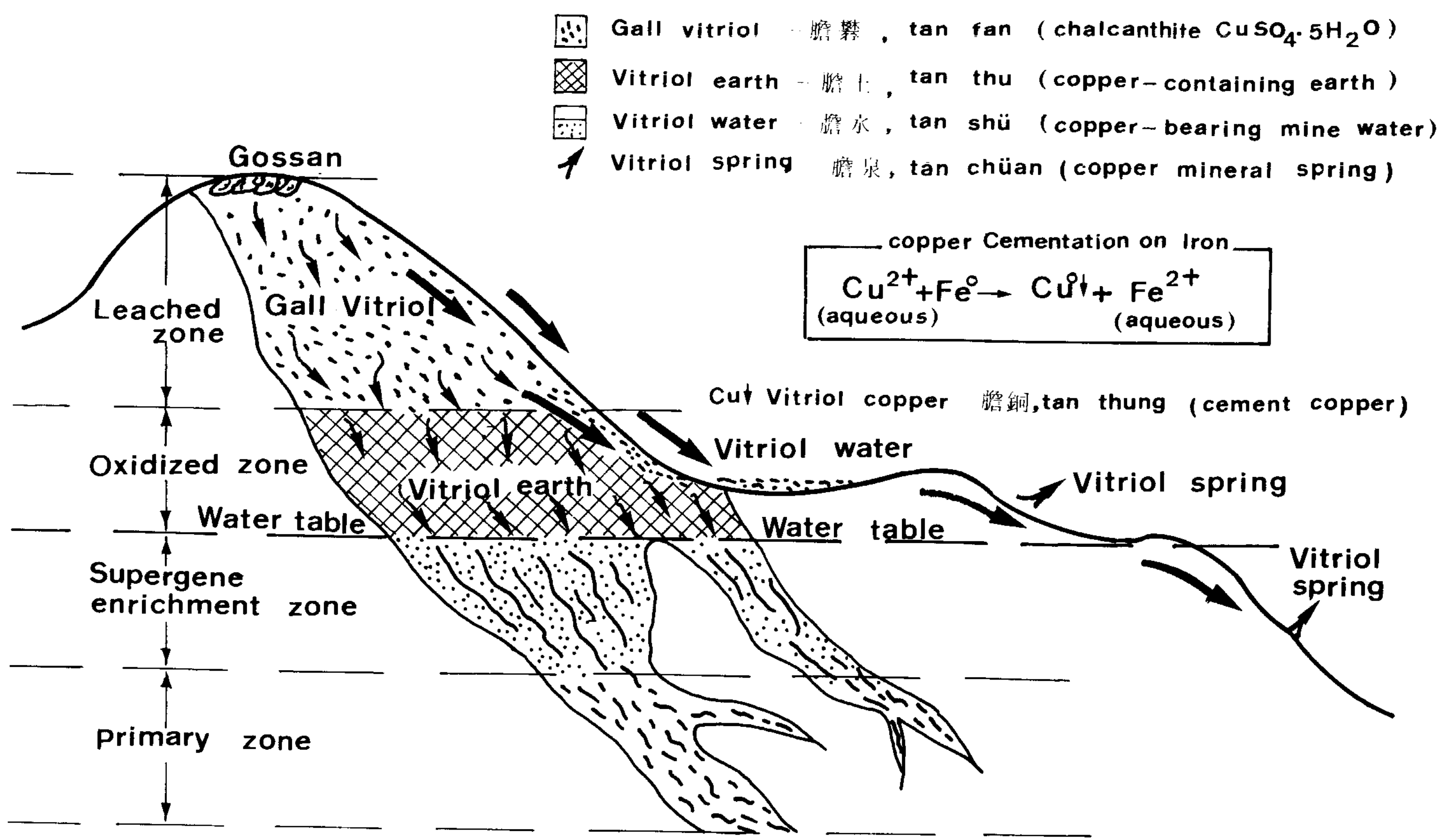


Fig. 3. Diagram of a weathered copper deposit with leached, oxidized, supergene enrichment and primary zones.

pits full of vitriol water, and others that were dry, but all the earth around them contains vitriol, so it is called 'vitriol earth' (*tan thu*)[i]. While it saves labour and gives more profit to use vitriol water, less satisfactory results can still be obtained by using the vitriol-containing earth. After all, though the water can be exhausted, this earth is available in plenty. So three officials of the Bureau of Forestry were appointed to search everywhere for vitriol waters and places where they had formerly been, so that profit could be obtained from both earth and water.

The statement in the book is a clear reference to the cementation of copper on iron from natural vitriol-bearing waters and vitriol-containing earth as well. More clearly it is mentioned that the process was applied for commercial production of cement copper. However, the earliest application of the process is still uncertain.

Weathering or natural oxidation of sulfide materials by the combined action of water, air, and ferric salts in solution is a slow process for transforming the copper sulfide minerals into water-soluble minerals. Where the copper deposit has undergone long-continued weathering, a zone of oxidation is normally formed on the surface; colourful ground has attracted the curiosity of miners from the earliest times. Seeping water with dissolved copper formed by such a natural process is very common in many copper districts. Figure 3 illustrates a weathered copper deposit showing the different zones including those where the copper-bearing water and earth are formed.

INDUSTRIAL APPLICATION OF THE PROCESS IN MEDIEVAL CHINA

The winning of metallic copper by precipitation from solutions of its salts in the presence of metallic iron is the first-known hydrometallurgical process; it has a history of more than 900 years. The operation is simple: copper-bearing water from mines or weathered copper deposits is allowed to flow over iron and to deposit copper by means of the exchange reaction between metallic iron and cupric ions in the solution. The industrial use of the process began in the early years of the Northern Sung period (960—1126 A.D.) and came into extensive use from the 11th century onward. In the *Sung Shih* (History of the Sung Dynasty) [11], we read:

The method of 'steeping copper' (*chhih thung*)[j] is to make (literally 'forge') thin plates of cast-iron and immerse them in rows in troughs of blue vitriol solution (*tan shui*)[h]. After some days a layer of red powder is formed by the copper sulphate over the surface of the iron; this is collected by scavenging and after three purifications in the furnace gives good copper. Broadly speaking, for every catty of copper 2.25 catties of iron are needed. The Hsing-li Mine at Jao-chou and the Chhien-shan Mine at Hsin-chou produced a definite amount of this 'vitriol copper' (*tan thung*)[k] each year.

This refers to 1143 A.D., but is based on long experience of cementation operations in earlier years. Theoretically, the amount of iron required to precipitate 1 kg of copper is 0.88 kg, but in practice iron consumption is much higher, between 1.5 and 4.0 kg per kilogramme of copper. The excessive consumption of iron is induced by side reactions; for instance free acid and ferric ions can react with iron too. So an iron consumption ratio of 2.25 as mentioned in the *Sung Shih* is reasonable and falls in the normal range.

In the years between 1094 and 1097 A.D., a book entitled *Chhin Thung Yao Lueh* (Important Aspects of Steeping Copper), a kind of operations manual, was written by Chang Chhien, a professional on copper cementation. This must be the first book on cementation anywhere in the world. Unfortunately, the book is no longer extant and only its preface has been conserved. Wei Su's (1307—1372 A.D.) preface was written in 1352 A.D., about 250 years later than the date of the book. The preface says:

> Chang Li (a man of Te-hsin), after being transferred to the Capital from his official post in Fu-chien, submitted his ancestor's book *Chhin Thung Yao Lueh* (Important Aspects of Steeping Copper) to the government just at the time when the State was reforming its currency policy. The Premier, considering the book beneficial to the national economy, reopened the Hsin-li Mine for him. One day in March 1352 A.D., the Premier requested His Majesty to appoint Chang Li as the officer in charge of the mine. He brought a copy of the book and asked me for a preface. My preface is: Using metal coins is now in favour. The amount of copper needed for smelting and casting is unlimited, but there is a limitation on copper production. Chang Li knows the method of steeping iron to produce copper. This method costs less than smelting and can make a large profit, so it must be good news to the government. In the prosperous period of the Sung dynasty, a government treasurer (Hsu Shen) knew the way to transmute iron to copper by applying drugs. After a long period, the operation was ended owing to the workers being unable to sustain the hardship of the job. The present book was written during the reign of Shao-shen (1094—1097 A.D.). The process has been established ever since. In 1086 A.D., the steeping of iron in vitriol springs (*tan chuan*[o]) to produce copper for smelting involved a total of 32 springs: 1 of them washing-off copper every five days (namely, Yuang-chung etc.), 14 of them washing-off copper every seven days (namely, Yun-fu, etc.), and 17 of them washing-off copper every ten days (namely, Si-jao-yuan etc.). In total there were 138 flumes. In 1115 A.D., heavy rainfall made the springs overflow, and the copper produced in that year from steeping reached a record quantity . . .

The preface indicates that the first commercial operation to extract copper by iron from a vitriol spring took place in 1086 A.D. The operation was carried out using ground flumes and copper was washed-off after fixed intervals of several days. Since then the technique has been applied in many copper mines in China and has continued for several hundred years.

The total production of vitriol copper (cement copper) in China during a year within the reign of Shao-hsing (1131—1162 A.D.) of the Sung dynasty reached 1,874,428 catties (equivalent to 1,124,657 kg). This is clearly recorded in the book *Sung Hui Yao Chi Kao* (Edited Manuscripts of the Essentials of the Sung Dynasty) [2] under the Shih-Ho Chih (Food and Treasure Section). There were four major mines producing cement copper at that time, namely: Hsin-li, Chhien-shan, Tsheng-shui and Yung-hsing Mines. The iron needed for copper cementation was supplied by iron smelters not far from the cementation plants. The statistics of Chinese cement copper production and related data for the 12th century are compiled in Tables 1 and 2 from the sources of *Sung Hui Yao Chi Kao* (Edited Manuscripts of the

TABLE 1

The production of vitriol copper (cement copper) in China in a peak-year during the reign of Shao-Hsing (1131—1162 A.D.) of the Sung dynasty

Mine	Location		Annual Production catty (kg)	Remarks
	Archaic	Modern		
Hsing-li Mine (興利場)	Jao-chou (饒州)	Kiang-hsi (江西)	51 030 (30 618)	1). All for coinage.
Chhien-shan Mine (鉛山場)	Hsin-chou (信州)	Kiang-hsi (江西)	380 000 (228 000)	2). Total copper produced in this year is 6 985 243 catty (4 191 146 kg), and vitriol copper in total is about 25%.
Tsheng-shui Mine (岑水場)	Shao-chou (韶州)	Canton (廣東)	800 000 (480 000)	
Yung-hsing Mine (永興縣)	Than-chou (潭州)	Hu-nan (湖南)	640 000 (384 000)	
Thung-lin Hsien (銅陵縣)	Chhih-chou (池州)	Che-kiang (浙江)	1 398 (839)	
Yung-kuang Hsien (永廣縣)	Wu-chou (婺州)	An-hui (安徽)	2 000 (1 200)	
Total			1 874 428 (1 124 657)	

1 catty (of the Sung dynasty) = 596.82 g ≈ 0.6 kg.
Source: Ref. [2].

TABLE 2

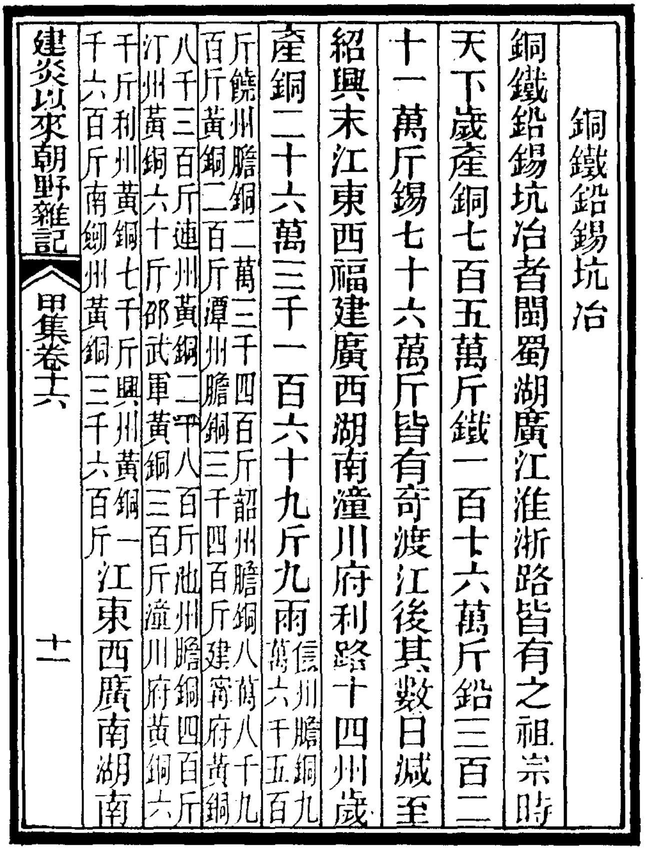
The historical statistics related to vitriol copper (cement copper) production during the 12th century in China

Unit: catty (kg)

Item	Annual Production	
	Peak Year	c. 1162
Vitriol copper(copper from solution)	1 874 428 (1 124 657)	212 600 (127 560)
Yellow copper(copper from ore)	5 181 835 (3 109 101)	29 860 (17 916)
Unrecorded(balance)	1 001 (600)	20 710 (12 426)
Total copper produced	7 057 264 (4 234 358)	263 170 (157 902)
Vitriol copper in total (%)	~25	~81
Total iron produced	2 162 144 (1 297 286)	
Iron consumed for steeping copper (copper cementation)		880 063 (528 038)

1 catty (of the Sung dynasty) = 596.82 g ≈ 0.6 kg.
Source: Refs. [2, 12].

Essentials of the Sung Dynasty) [2] and Li Hsin-Chhuan's *Chien-Yen I Lai Tskao Ye Tsa Chi* (Miscellaneous Records of Official and Unofficial Affairs Since Chien-Yen's Reign) [12]. A page related to vitriol copper (cement copper) production from Li Hsin-Chhuan's book is reproduced as Fig. 4.



銅鐵鉛錫坑冶

銅鐵鉛錫坑冶者閩蜀湖廣江淮浙路皆有之祖宗時天下歲產銅七百五萬斤鐵一百七十六萬斤鉛三百二十一萬斤錫七十六萬斤皆有奇渡江後其數日減至紹興末江東西福建廣西湖南潼川府利路十四州歲產銅二十六萬三千一百六十九斤九兩信州膽銅九萬六千五百斤饒州膽銅二萬三千四百斤韶州膽銅八萬八千九百斤黃銅二百斤潭州膽銅三千四百斤建寧府黃銅八千三百斤連州黃銅二千八百斤池州膽銅四百斤汀州黃銅六十斤邵武軍黃銅三百斤潼川府黃銅六千斤利州黃銅七千斤興州黃銅一千六百斤南劒州黃銅三千六百斤江東西廣南湖南

建炎以來朝野雜記 甲集卷十六 十二

Fig. 4. The production record of copper and cement copper of the year c. 1162. From Li Hsin-Chhuan's (1166–1243) *Chien-Yen I Lai Tskao Ye Tsa Chi* (Miscellaneous Records of Official and Unofficial Affairs Since Chien-Yen's Reign), written 1202 [12].

Since copper sulphate (vitriol) has an astringent and acrid taste, and shows a colour of blue to dark blue, it is similar to animal's gall. So in Chinese, traditionally, all compounds related to copper sulfate are called *tan* (literally 'gall'), for instance, mineral chalchanthite ($CuSO_4 \cdot 5H_2O$) is *tan fan*[g] (gall alum), aqueous solution of copper sulfate is *tan shui*[h] (gall water), a spring bearing copper salts is *tan chüan*[o] (gall spring), earth containing copper sulfate minerals is *tan thu*[i] (gall earth), and copper extracted from copper sulfate solutions is *tan thung*[k] (gall copper). The operation to precipitate copper is called *chhin thung*[j], which means immersing copper in water. Leaching copper from vitriol-containing earth to make copper solution for cementation is called *lin thung*[n], which means sprinkling copper. These terms had been used for many centuries until Western science and technology were introduced into China in the late 19th century.

During the Sung period (960–1279 A.D.), copper was not only recovered in large-scale operations in many places from groundwater containing copper

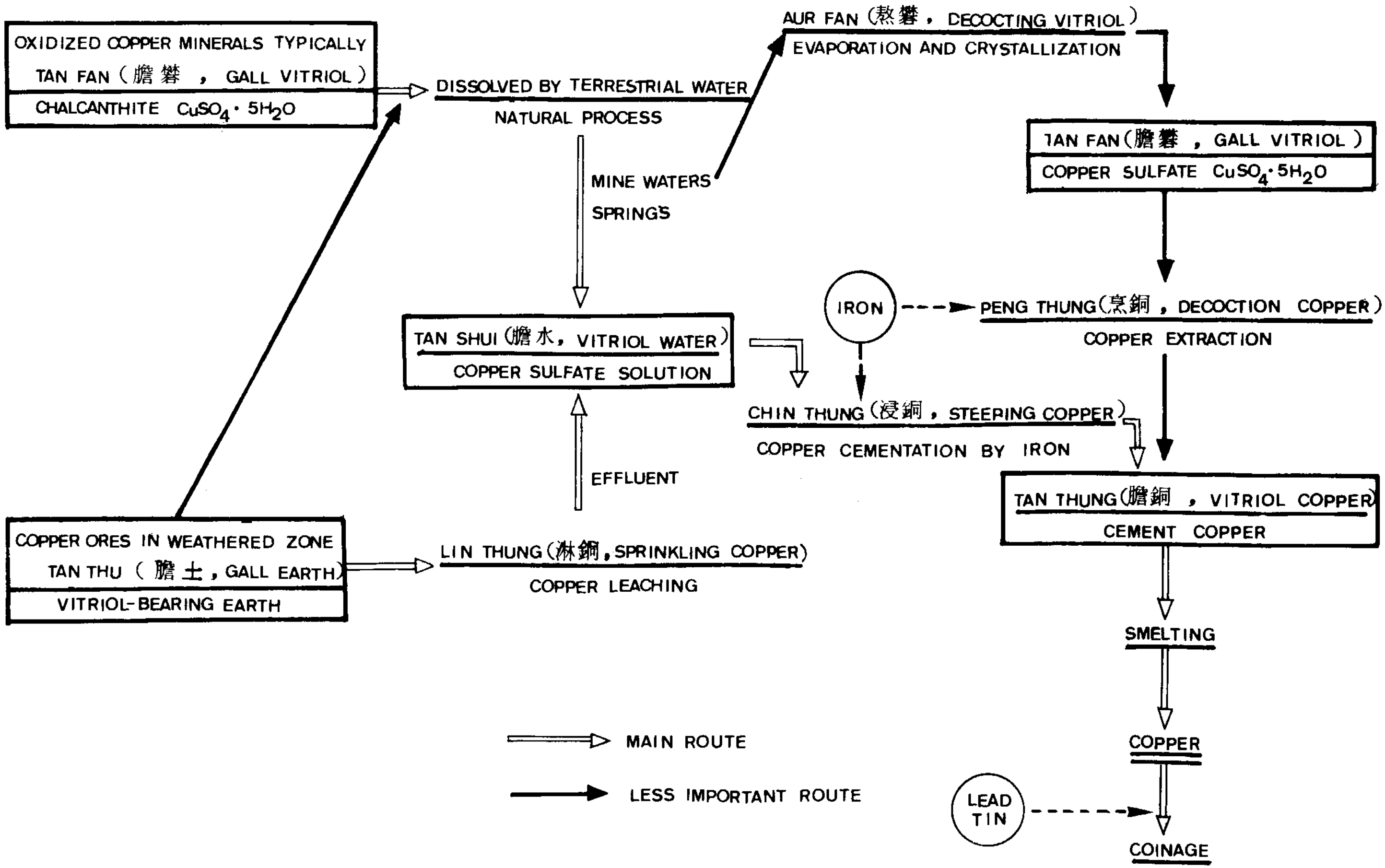


Fig. 5. Flow chart of production and utilization of cement copper in China between the 11th and 12th centuries.

salts, but leaching was also employed to dissolve water-soluble copper minerals in earth to prepare copper solution for cementation. The method of cementation by using ground flumes can be found in *Sung Shih* (History of the Sung Dynasty) [11], *Sung Hui Yao Chi Kao* (Edited Manuscripts of the Essentials of the Sung Dynasty) [12], Ku Tsu-Yu's *Tu Shih Fang Yu Chi Yao* (The Historian's Geographical Companion) [13], and Wang Hsiang-Chih's *Yu Ti Chi Sheng* (Places of Geographical Importance) [14]. Figure 5 is a flow chart of the different ways of producing and using cement copper in China between the 11th and the 12th centuries.

From the 12th century onward, cement copper production in China declined and gradually faded away. The reasons were inadequate supplies of natural copper solutions, scarcity of vitriol-containing earth, and diminishing copper demand due to the use of iron coins and later paper currency gradually becoming popular in China. Under the Yuan dynasty (1279—1368 A.D.) and the following Ming dynasty (1368—1644 A.D.), the use of the cementation process to produce copper was continued but only on a relatively small scale, if not completely stopped. However an important discovery was made in the 15th century. It was found in China that not only iron but also metallic lead and tin can be used to precipitate copper from solutions of its salts. In *Shih-Tien Tsa Chi* (Miscellaneous Notes of Stone-Field) [15], Shen Chou (1427—1509 A.D.) tells us:

> At Thung-ching (Copper Well) in Chhien-shan (Lead Mountain) of Hsin-chou, Kiang-hsi (Western Yang-tze River Region), the mountain produces *kung ching*[l] (azurite) and the water colour of the well shows navy-blue. When lead and tin are steeped in the water for two days and two nights, *hei hsi*[m] (black tin) is formed. After heating the *hei hsi*, it yields copper.

This is true because lead and tin are more electropositive than copper. Throughout the whole Ching dynasty (1644—1911 A.D.), there is no literary mention of copper cementation. Nevertheless, copper cementation regained its reputation in China in the middle of the 20th century as the most economical method of producing copper. At the Chin-kua-shih Mine of the Taiwan Metal Mining Corporation, Taiwan, the total amount of cement copper produced from 1944 to 1982 is about 29,000 tons. This corporation is the largest producer of cement copper ever to exist in China. The 900-year old traditional Chinese technique, using ground flumes, is applied almost unmodified in the Chin-kua-shih Mine. The only difference is the use of scrap iron instead of virgin iron. In July 1982, the production of precipitated copper from mine drainage water ceased owing to the economically unworkable low copper-content in the solution.

BRIEF HISTORY OF COPPER CEMENTATION IN THE WESTERN WORLD

About 1500, Basil Valentine, in his book *Currus Triumphalis Antimonii*, referred to copper cementation. Similarly, Paracelsus the Great (1493–1542) referred to the process as being a result of alchemical operations in the *Book Concerning the Tincture of the Philosophers*. There is some indication that the process as described by Paracelsus may have been a commercial means of producing copper. In *De Natura Fossilium* [16], published in 1546, Georgius Agricola (1494–1555, German) referred to the erosion of iron with mine waters for producing copper. The relevant passage is:

> At Smolensk, a town in the Carpathian mountains in that part of Hungary that was called Dacia at one time, water is taken from a certain pit and poured into canals that are grouped in series of three. Pieces of iron laid along these canals are turned into copper. Very small pieces of iron that are placed at the ends of the canals are eaten by the water in such a fashion as to give the iron a yellowish colour. This copper is refined in a furnace. Water similar to that mentioned above also drops from veins filled with minerals that are joined by a natural relationship to *atramentum sutorium* and from which the latter is produced as I have mentioned elsewhere.

Rio Tinto in Spain produced copper commercially by precipitation (in Spanish, *cementation*) on iron in the sixteenth century, and yearly production in 1833 was 140 tons. By the nineteenth century cement copper was produced commercially in Ireland, England, Germany and Hungary. Undoubtedly, by this time the production of copper by cementation on iron was widespread throughout Europe. Sponge iron, prepared by low-temperature reduction of hematite, was first tried as a precipitant for copper in England in 1837. By 1875 cement copper produced in Hungary amounted to 200 tons per year. In the United States copper concentration was carried out on water pumped from Butte Mines, Montana, in 1888, although it was not commercially successful until 1901. In 1910 copper-bearing water at Butte produced 2279 tons of copper by precipitation on scrap iron. The procedure applied at the High Ore Plant, Butte, Montana in 1903 is briefly described as follows [17]:

> The amount of water flowing averages 1200 gallons per minute. The average copper content is 0.05 per cent, and the extraction is 98.6 per cent. On leaving the mine, the water passes through the first set of flumes, three in number, parallel to each other, each 4 feet wide, 2 feet deep, and 300 feet long, with a fall of 2 per cent. These flumes are filled with scrap iron, such as rails, pipes, rods, and bars. The iron is continually turned over in order to dislodge the precipitate. Every few days one of the flumes is cut out of circuit, so that the iron may be temporarily removed and the precipitate washed into the settling tanks at the end of the flumes. The water afterwards passes down a second series of flumes, 8 feet wide, with an incline of 2½ per cent, and length of 500 feet. Along these flumes there are settling tanks spaced 75 feet apart. The settling tanks are large wooden boxes, of the same width as the flumes, about 15 feet long and 8 feet deep, and so arranged that the precipitate can be sluiced through a hole in the bottom into drying vats. After passing through the flumes, the water is pumped to towers and subsequent flumes for secondary extrac-

tion. Roughly 95 per cent of the copper content is recovered in the flumes before going to the secondary circuit. The cement copper after being air-dried contains approximately 70 per cent Cu.

For many centuries copper precipitation on iron was carried out in trough cementators of various types; a copper yield of 97% could be achieved in suitable operating conditions. Many different types of equipment for cementation such as drums, tanks, and cells, have been developed in recent years. One of the most important developments is the cone-precipitator which was developed in the United States by Kennecott Copper in the 1960s [18]. Fundamentally, all types of equipment are operated on the same basic principle, using iron to displace copper in solution; only the form used differs. Now the principal trend in recovering copper from solutions is the gradual conversion from iron cementation to solvent extraction—electrowinning, which is a process developed from modern chemistry and hydrometallurgy. After 900 years of service, the importance of copper cementation on iron is diminishing, but may never vanish altogether.

CONCLUSIONS

Cementation, or contact precipitation, is a process that has been used for nine centuries to deposit cement copper from solution with metallic iron as reductant. The process has been applied successfully in China to win copper from natural copper-bearing solutions since 1086 A.D. This is about five centuries earlier than in Europe or elsewhere. From the 16th century on, the technique has been used widely in most of the world's districts. For many centuries, the copper cementation process has been a very effective and economic, as well as the simplest method of extracting copper from solutions, but now it is gradually being replaced by other modern technologies. The recognition of the reaction that iron can be converted to copper is a contribution of ancient Chinese alchemists through their alchemical practices within the years roughly between the 2nd century B.C. and 2nd century A.D. The precipitation of copper on iron is a classic example of an ancient art that has been applied successfully for many centuries with little fundamental understanding of the important parameters involved.

EXPLANATORY NOTES

a. *pei ching*(白青, pale green): a weathered greenish mineral, most probably brochantite (basic copper sulfate, $Cu_4(OH)_6SO_4$).
b. *shih tan* (石膽, stone gall): chalcanthite ($CuSO_4 \cdot 5H_2O$).
c. *fan-shih shui* (礬石水): aqueous solution of *fan shih* (alum stone).
d. *fan shih* (礬石, alum stone): a mineral of alum, most probably a copper-bearing mineral of iron sulfate.

e. *hua chhih* (華池, dissolving pool): vinegar pool.

f. *chi-shih fan* (雞屎礬, chicken-dirt alum): a copper mineral, uncertain, may be azurite, malachite, chrysocolla or a mineral substance of its sort.

g. *tan fan* (膽礬, gall vitriol): chalcanthite ($CuSO_4 \cdot 5H_2O$).

h. *tan shui* (膽水, vitriol water): natural copper sulfate solution, copper-bearing mine water.

i. *tan thu* (膽土, vitriol earth): vitriol-containing earth, earth containing copper sulfate minerals.

j. *chhin thung* (浸銅, steeping copper): copper cementation from solutions of copper salts by iron.

k. *tan thung* (膽銅, vitriol copper): cement copper.

l. *kung ching* (空青, empty green): probably azurite [$Cu_3(CO_3)_2$-$(OH)_2$].

m. *hei hsi* (黑錫, black tin): metallic copper.

n. *lin thung* (淋銅, sprinkling copper): copper leaching.

o. *tan chüan* (膽泉, gall spring): vitriol spring, springs containing copper sulfate.

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