

# Chemistry Progress and Civilization in Ancient China

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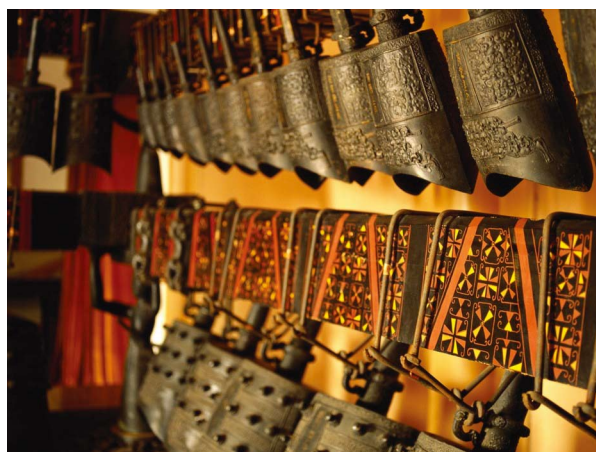
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During the 6,000 years of Chinese civilization, chemistry has played an essential role. The bronzed chime bells of the Warring States Period (475–221 BC) unearthed in Hubei Province shows not only the excellence in musical instruments in ancient China, but also the technological advances in metallurgy. Chinese alchemy was not originated from the quest to turn common metals to gold, instead, it was for searching medicines for longevity of human beings, mostly practised by Taoists. Such efforts led to the discoveries of gunpowder in the Tang Dynasty (618–907 AD) as well as several types of Chinese medicines, which have benefited the Chinese people's health for thousands of years. We will discuss the evolution of pottery, porcelain, glaze, dyes and pigments with improved chemical compositions.

## 1. Metallurgy

During the Beijing 2008 Olympic Games, the music *Molihua* played during the medal ceremonies deeply touched audiences. The beautiful principal melody was played on the chime bells (*Bianzhong*) of Marquis Yi of Zeng, a complete set of percussion instruments made from bronze in 433 BC. Unearthed in 1978 from Zenghouyi Tomb in Sui County, Hubei Province, China<sup>[9]</sup>, its excavation has astounded the world. It is extremely rare in the world cultural history to find such exquisite musical instruments of over 2,000 years ago, and the chimes can still be played with a beautiful timber and wide range after being buried for so many years. It is the embodiment of our great achievement in bronze casting, our proficiency in music science and the wisdom of our people in ancient China.

Actually, Chinese people used copper to cast matter more than 4,000 years ago<sup>[13]</sup>, and the ancient copper products range from weapons to daily living articles. An



A set of ancient chime bells.

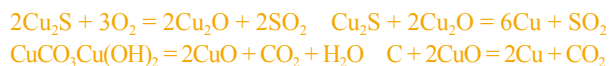
analysis of ancient Chinese documents and copper antique compositions shows that, besides using natural pure ores directly, ancient Chinese smelters had grasped smelting technology of various copper alloys, such as bronze, brass and white-copper.

Bronze is a metal alloy consisting primarily of copper, usually with tin as the main additive. Weighing 832.84 kg, the *Simuwu* (*Houmuwu*) tetrapod is the heaviest ancient bronze ware in the world. It consists of 84.8% copper, 11.6% tin, 2.8% lead, *etc*<sup>[13]</sup>. As one of the most significant collections at the National Museum of China, it symbolizes the blossom of bronze culture in the Shang and Zhou Dynasties (*c.*1700–771 BC). After that, many other styles of bronze items were invented as time went by. The famous painting *Wise and Benevolent Women* by Gu Kaizhi around 400 AD illustrates that the bronze mirror became a daily necessity for ancient Chinese females.

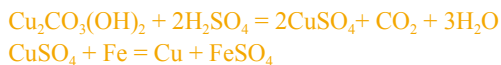
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Paktong, another type of copper alloy, was first known in China ca. 300 BC<sup>[5]</sup>. It is an alloy of copper with large amount (about 25%) of nickel, so that paktong is also known as cupronickel. Because of its color, Chinese call it “white copper” as well. In fact, white copper still refers to another type of copper alloy — arsenic copper in China<sup>[13]</sup>. The paktong coins “*da xia zhen xing*” casted by the creator of Huxia Counties, Helian Bobo, during the Sixteen Countries Period (304–420 AD), is famous among the numerous ancient coins

How did ancient people smelt copper? The Chinese encyclopedia *Tiangong Kaiwu* wrote by Song Yingxing (1587–1666 AD) documented the copper smelting technology. From the pictures illustrated in the book, it is easy to find that the process of smelting copper is mining copper ores, and putting them in the special smelting furnace to be heated in air. Copper minerals for producing copper were commonly malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ) and chalcocite ( $\text{Cu}_2\text{S}$ )<sup>[8]</sup>. The main chemical reactions are listed below:



In the Western Han Dynasty (206 BC–8 AD), copper hydrometallurgy was first invented in China<sup>[13]</sup>. Copper hydrometallurgy is concerned with processes involving aqueous solutions to extract copper from its soluble ores, such as malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ) and atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ). The chemical reactions are the following:



Especially in the Southern Song Dynasty (1127–1279 AD), the yields of copper hydrometallurgy accounted for 15% of the total output<sup>[4]</sup>. Zhang Qian (1025–1105 AD) largely contributed to the development of the hydrometallurgy for large scale production. After him, the proportion of hydrometallurgy of copper increased from less than 20% to 80%. China’s invention of copper hydrometallurgy, about 800 years earlier than Europe, was a



Illustrations from *Tiangong Kaiwu*, showing (a) Mining copper ore; (b) smelting copper ore and the process of removing lead elements



*Simuwu (Houmuwu)*, a bronze sacrificial vessel, casted by a king of tribe in memory of his mother in the late Shang Dynasty.



*Wise and Benevolent Women*, by Gu Kaizhi in the Eastern Jin Dynasty (c.348–409), illustrates that the bronze mirror became a daily necessity for women.

big contribution to the world copper metallurgy.

Iron is better than bronze in terms of strength and hardness, which was known to Chinese several thousand years ago. A bronze tomahawk of the Shang Dynasty (c.1600– 1046 BC) was excavated in Hebei Province in 1972<sup>[13]</sup>. Its meteoritic-iron edge demonstrates that, as early as 3,300 years ago, Chinese had mastered the iron forging technology.

Around 500 BC, in Wu Kingdom, it was achieved in the iron smelters a liquid cast iron with 4.3% carbon. In liquid state, iron can be cast into molds, which is a far less laborious method than forging each piece of iron from a bloom. When it came to Warring States Period, Chinese metallurgists realized that cast iron is rather brittle, unsuitable for usage of strong striking, then they





(a) An iron-bladed bronze tomahawk in Shang Dynasty; (b) a bronze-handled iron sword of the Spring and Autumn Period (722–479 BC), indicating Chinese had begun smelting cast iron from that time at the latest.

found that cast iron could be decarburized by heating it in air for several days. As a result, wrought iron with less carbon containing was made. Meanwhile, malleable cast iron possessing a good ductility was achieved as well. Until the Han Dynasty (206 BC–220 AD), iron metallurgy had reached its peak<sup>[17]</sup>. Various smelting methods were invented, including hundredfold steel smelting, puddling steel smelting and perfusing steel<sup>[3]</sup>. During this period, large blast furnaces were built to produce iron. Later, furnace bellows operated by waterwheels were invented, which can be regarded as a first example of green chemical engineering. The *Tiangong Kaiwu* also recorded iron smelting technology.

The general chemical process of iron smelting, for instance for hematite ( $\text{Fe}_2\text{O}_3$ ) is given by the following:



## 2. Alchemy and Chinese Medicine

Chinese alchemy, as a part of the larger tradition of Taoism, focused mainly on the purification of one's spirit and body in the hopes of gaining immortality through the use of various concoctions known as alchemical medicines or elixirs, each of which having different purposes. It is different from the alchemy in other cultures, which was to search for the transmutation of common metals into gold

<sup>[18]</sup>. The legendary founder of alchemy is Qin Shi Huang, the very first emperor of the unified China (221 BC). At the later stage of his life, the emperor feared death and desperately sought the fabled elixir of life, which would supposedly allow him to live forever<sup>[19]</sup>.

Even though their destination was unreachable, Chinese alchemists created some useful alchemical medicines with chemical methods, such as realgar ( $\text{As}_4\text{S}_4$ ), mercury (Hg) and tin (Sn)<sup>[1]</sup>. According to the *Bencao Gangmu*, or *Compendium of Materia Medica*, written by Li Shizhen (1518–1593 AD), in Ming Dynasty (1368–1644 AD), realgar was utilized as disinfectant for treating acne. Another medical book *Tangcaomu* in the Tang Dynasty records “silver paste”, a kind of mercurial made from mercury, silver and tin, which was used to fill a tooth<sup>[15]</sup>. So to that extent, we can say that Chinese alchemy technology had stimulated the development of the ancient civilization in China.

Chinese herbal medicine has played an essential role in continuing the Chinese civilization and guaranteeing people's health. *Bencao Gangmu* is regarded as the most complete and the most comprehensive medical book in the history of Chinese herbal medicines. There are totally about 2-million Chinese words, with 1,160 hand-drawn illustrations, 1,892 distinct herbs (of those 374 were added by the author) and 11,096 prescriptions (8,160 by the author). It is still regarded as the most important Chinese medicine classical work. It is no doubt that Chinese herbal medicine needs to be improved by modern science and technology. On the other hand, modern science also has a lot to learn from the traditional medicine. The example of *qinghaosu* (artemisinin) well illustrates such relationship. Qinghao (artemisia) was used by ancient Chinese as an antimalarial herb, which was documented in the “Fifty-Two prescriptions” (200 BC), unearthed in 1972 from Ma Wang Dui Han Dynasty Tombs in Changsha. Qinghao was isolated from Qinghao leaves in 1972 by Chinese scientists, Tu Youyou and coworkers. Nowadays, *qinghaosu* and its derivatives have been widely employed in modern chemical medicine.



*Bencao Gangmu* (*Compendium of Materia Medica*), the comprehensive Chinese herbal medicine classical work; (b) Portrait of the author Li Shizhen (c. 1518–1593).

### 3. Gunpowder

As one of the Four Great Inventions in ancient China, gunpowder was first produced in the Tang Dynasty in the 9th century. In fact, it was invented by Chinese alchemists to find elixir of immortality. The first document mentioning gunpowder was possibly a passage in the *Zhenyuan miaodao yaolie*, a Taoist book dated to the mid-9th century<sup>[12]</sup>.

Gunpowder here refers to black powder, which is a mixture of sulfur, charcoal and potassium nitrate. It is different from other types of gunpowder, such as smokeless powder. Combustion of this gunpowder is a complex process of chemical reactions. When being burned, it produces a volume of hot gas made up of carbon dioxide, sulfur dioxide, water, nitrogen, and a solid residue of potassium sulfide<sup>[20]</sup>. A simple and commonly cited chemical equation for the combustion of black powder is:



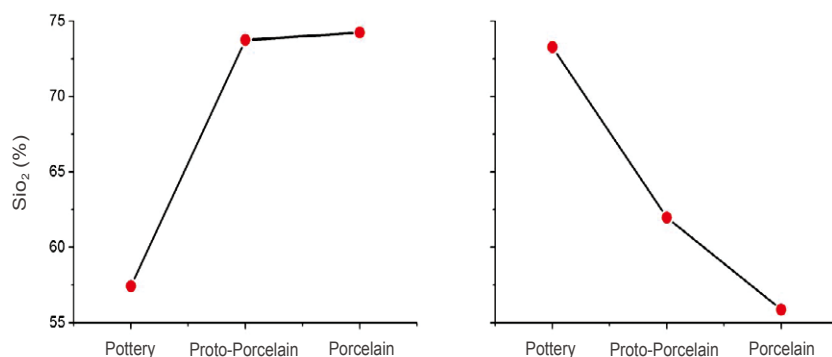
Because of the amount of heat and gas rapidly produced during the burning reaction, gunpowder is classified as an explosive and has been applied widely to firearms and fireworks 1,000 years ago in China. It is said that military of Tang in 906 had used the incendiary projectiles with bows and arrows called *fei huo*, literally flying fire, to attack cities of an enemy. The earliest depiction of a gunpowder weapon is a mid-10th century silk banner from Dunhuang that shows a fire lance which is the precursor of gun, a finding of the famous scientist, historian, and sinologist Prof. Sir Joseph Needham<sup>[25]</sup>. Then, many more types of weapons were invented, such as fuel rockets, fire-guns, cannons and bombs. The gunpowder recipes and technique can be found in several documents, such as *Wujing Zongyao* written in the Song Dynasty<sup>[12]</sup>. Besides, gunpowder was also utilized in fireworks in Ming Dynasty<sup>[14]</sup>. During the opening ceremony of Beijing 2008 Olympic Games, the gorgeous fireworks have been so much exciting!

From 1225 to 1248 AD, gunpowder technique was spread to the Arab World and Egypt. Then it went to Europe from Arab during the Renaissance. North Korea imported gunpowder from China around 13th Century. Meanwhile Chinese people migrated to the Southeast Asia and took gunpowder technology there. In the 16th century, it reached Japan because of pirates<sup>[6]</sup>. Therefore, the discovery of gunpowder by ancient Chinese has a far-ranging global impact.

### 4. Pottery and Ceramics

The earliest known pottery dated back to 11,000 years ago, during the Paleolithic Era. The birth of pottery started from making use of fire by the Yuanmou Man (*Homo erectus yuamouensis*). It was found that the clay would be solid after being heated by fire.<sup>[13]</sup> Pottery pots of the Dawenkou Culture (4300–2500 BC) have been excavated from Tai'an, Shandong Province. In the Shang and Zhou Dynasties (c. 1600–256 BC), people began to pursue better ceramic quality. And they found that characteristics of ceramics could be improved by using selected raw materials and advanced ceramic technology. As a result, proto-celadon and porcelain emerged in 1300 BC and 200 AD, respectively. Nowadays, scientists have found<sup>[7]</sup> the increased proportion of SiO<sub>2</sub> and the decreased proportion of Fe<sub>2</sub>O<sub>3</sub> in pottery, proto-celadon to porcelain, successively. As SiO<sub>2</sub> increases, the mechanical strength of ceramic improves while as Fe<sub>2</sub>O<sub>3</sub> decreases, the whiteness and transparency are enhanced. A proto-celadon ware, a wine vessel with a dragon-shaped handle — made in the Warring States Period, was unearthed in Shaoxing, Zhejiang Province in 1955, it is the symbol of proto-celadon in early period of China.

Besides promoting the strength and transparency of ceramics, ancient Chinese still tried to beautify them. Glazes were widely employed, which are layers or coatings of vitreous substances, fused under fire into ceramic object



A Composition of SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> in pottery, proto-celadon, and porcelain.



A Bo-shaped pottery "Ding" (tripod) from the Dawenkou culture, c. 4300–3500 B.C. On display at the Shanghai Museum.



to color, decorate, strengthen or waterproof it <sup>[21]</sup>. Glazes contain colorants, such as  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{MnO}_2$ , to make ceramics elegant and beautiful. And Tang Sancai developed in the Tang Dynasty belongs to another type. Tang Sancai literally means three colors of Tang dynasty, yellow, green and white, but not limited to these three. Sancai travelled along the Silk Road, and the similar styles can be also found in Syrian, Cypriot, and then Italian pottery from the 13th to the middle of the 15th century. Sancai also became a popular style in Japanese and other East Asian ceramic arts. <sup>[24]</sup>

### 5. Pigments and Dyeing Techniques

As early as the Western Zhou Dynasty (1046–771 BC), the technologies of dyeing and weaving had already produced big influence in China. *Li Ji (the Book of Rites)*, one of the five Confucius canons, described the social and governmental systems, as well as ceremonial rites of the Zhou Dynasty. It documented that there were already special officers in charge of weaving and dyeing in the administration.

As a special resist dyeing technology, batik is applied by ethnic minorities in Guizhou Province <sup>[15]</sup>. As early as in the Han Dynasty, the Miao, Bouyei and Gejia peoples developed a dye resist method for their costumes, which use knives for waxing to draw patterns on hemp and cotton before dyeing. The common dye used in batik is indigo ( $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ ), a natural blue dye <sup>[10]</sup>.

The colorful Buddhist mural art illustrates that ancient Chinese knew the usage of pigments more than



A batik work in Miao nationality of Guizhou Province.



(a) Wall Painting in Tang Dynasty from Cave No. 112, depicting a pipa-playing Buddhist semi-deities (b) A 10th century mural from Cave No. 61, showing Tang Buddhist monasteries of Mount Wutai, Shanxi province

1,000 years ago. According to an analysis of the Mogao Cave paintings <sup>[11]</sup>, the pigments there contained inorganic pigments, organic pigments and minerals. Some examples of inorganic pigments are red cinnabar ( $\text{HgS}$ ), yellow orpiment ( $\text{As}_2\text{S}_3$ ) and green verdigris ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ). Organic pigments include yellow gamboges, red cochineal and blue indigo. From the great arts in history, we could see that pigments and dyeing techniques have been indispensable to promote the progress of ancient Chinese civilization.

### 6. Alcoholic Beverages

As in many cultures, alcohol is important for both ceremonies and daily life. Chinese had mastered the technology to ferment fruit and produce fruit wine in ancient times. Then, around 6,000 years ago, Huangjiu, literally yellow liquor, made from fermented grain appeared. It is a type of Chinese alcoholic beverage brewed directly from grains, such as rice, millet, and wheat, and generally contains less than 20% alcohol by volume. The various styles of Huangjiu may vary in color from clear to beige, yellowish-brown, or reddish-brown. In the Tang dynasty,



distillation technique was developed to produce Baijiu, or white wine after fermenting of grains. Consequently, Baijiu is clear and its alcohol content is much higher than Huangjiu's<sup>[22]</sup>. The chemical reaction involved in producing alcoholic beverage is:



As one type of traditional Chinese liquor, Huangjiu has several varieties. Nu'er Hong (daughter red), originating from Shaoxing, Zhejiang province, is a special Huangjiu type. It is made of glutinous rice and wheat, and its alcohol content is 16% by volume. Besides drinking directly, Huangjiu can also be used in Chinese cooking and macerating herbs to make herbal medicine wine<sup>[23]</sup>.

Chinese liquor culture history is glorious, well-established. When special festivals came, people got together to eat and drink<sup>[2]</sup>. For instance, Chinese used to drink chrysanthemum wine in the Chongyang Festival. Even until now, beverages are still a significant part of our daily life.

## Conclusion

Contemporary chemistry only emerged in the 18<sup>th</sup> century in Europe. Though ancient Chinese did not know what electrons, atoms or molecules were, the progresses

made by our ancestors in metallurgy, medicines, black powders, ceramics and materials, pigments and dyes, and many others can be regarded as spontaneous achievements, which are now classified in the category of chemical sciences. Indeed, as expressed by the motto of International Year of Chemistry: Chemistry – our life, our future, China's achievements in the past do indicate that chemistry is a central science of life. And chemistry will continue to contribute to solve the global challenges in energy, environment, resources, and health. The famous American author and historian David McCullough once said: "History is a guide to navigation in perilous times. History is who we are and why we are the way we are". The reason we are telling the history of Chinese chemical science and technology here, is to remind all of us that chemistry has made great contributions in advancing the human civilizations and will lead us to a brighter future.

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