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Substance flow analysis of copper in production stage in the U.S. from 1974 to 2012

Minxi Wang, Wu Chen, Xin Li*

College of Management Science, Chengdu University of Technology, Chengdu 610051, PR China

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ABSTRACT

Substance flow analysis (SFA) provides a systematic framework for tracking the sources, pathway, intermediate and final sinks of copper in the United States. The stocks and flows (STAF) method compensates for the deficiency in statistics. This paper combines SFA and STAF method to reflect the realistic copper stocks and flows within production boundary from 1974 to 2012. The goal of this paper is to discern the evolution of the copper production industry in the U.S. when conditions require that industry operates with a lower-grade ore and more sustainable development concerns are considered. The emergence of the new solvent-extraction electrowinning (SX–EW) technology, which is used in conjunction with conventional extractive metallurgy, altered the structure of domestic refined copper production. Refined copper production declined after peaking at 2486 Gg/year in 1998. In 2012, primary production was only 45.02% of the primary production in 1998, and secondary production was only 10.69% of secondary production in 1998. The decrease is due to the decline in the primary and secondary copper sources for domestic use and closure of secondary smelting and refining facilities. A portion of the lower grade ore was exported through trade after 1998. More scrap was not delivered to produce refined copper. Closure of secondary smelting and refining facilities decreased the refinery scrap in a poor economic environment. Imported refined copper offset the gap due to the decrease in domestic refined copper production. The ratio of net imported refined copper to domestic refined copper increased from 9.97% in 1974 to 47.03% in 2012. The U.S. is more dependent on import of refined copper, except during the period in which a tight global copper market disrupted the leading copper-producing country.

1. Introduction

Copper is one of the early metals used by humans. Archeological evidence demonstrates that people in western Asia used copper at least 10,000 years ago. People began to exploit open-pit mines and use copper extracted from ore to produce weapons, tools, vessels, etc. before 6000 years ago (Li, 2010). Copper was widely distributed in nature, and, in the earth crust, it takes the following forms: sulfide ores (as chalcopyrite, bornite, chalcocite, and covellite), oxide ores (as cuprite and tenorite), saline minerals (as malachite, azurite, chrysocolla, connellite and antlerite) and native copper (Davenport et al., 2002). Copper and copper-based alloys are applied in five fields, including building construction, electrical and electronic equipment, industrial machinery equipment, transportation equipment and other uses, due to its corrosion-resistant, machinable, excellent conductive and malleable properties (International Copper Study Group, 2012).

Copper ores cannot be directly used in any fabrication and manufacture stage process, and they must be extracted through an extractive metallurgy technology to extract refined copper. In general, the process from copper mining to refined copper is referred to as copper production (in a subsequent paper, it is referred to as production). At present, copper is mainly extracted from most sulfide minerals through conventional pyrometallurgical processes. Otherwise, copper is extracted from oxide ores and a small portion of sulfide ores through a hydrometallurgical process referred to as a solvent-extraction electrowinning (SX–EW) process. The production phases of different periods feature certain significant differences. The first difference is the type of copper ores mined from different regions, and the second difference is production processing during different times with extractive metallurgy technology development. Due to these differences, consumption (such as raw material consumption and energy consumption) and certain environmental pollution problems also differ.

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* Corresponding author.
E-mail address: lixin2012@cdut.cn (X. Li).

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By observing industrialization of developed countries, these countries clearly developed an extensive economy at the expense of energy and the environment. After hundreds of years of exploitive mining and processing, industrialized countries intend to use technology with low energy consumption, low pollution and high economic efficiency due to economic and environmental pressure. Due to mining, processing, recycling, etc., the copper industry contributes to building infrastructure and creating trade and investment opportunities, which greatly contributed to the development of industrialization (International Copper Study Group, 2012). The newly industrialized countries require a great deal of metallurgical copper during the rise of industrialization, which may require energy consumption and greatly contribute to environmental pollution if they adopt a means of extracting metallurgy with high energy consumption. With a global focus on sustainable development, developing technology that extracts an equal quantity of copper with less energy consumed and environmental pollution has become a global concern. Copper production within a spatial boundary is the source for the copper used in society, which is critical to society. Further, copper production is complicated because different copper mineral species require different extractive metallurgy processes. Thus, the sub-process conditions during the production stage must be determined.

Substance flow analysis (SFA) can provide information on copper cycles with a framework, which may aid in discerning the input, output and change in copper flow conditions at different stages at the regional and country levels. The stocks and flows (STAF) method can support the SFA in reflecting the objective, real-world conditions. Exploiting industrialized countries in production phase may provide a reference for the newly industrialized countries and help them select economically efficient and less polluting technology.

Thus, this paper emphasizes analyzing copper processing within the production boundary by combining an SFA and the STAF method as the framework. By analyzing copper from 1974 to 2012 under an SFA framework, the change in copper stocks and flows for the several specific years used in this paper is easily determined. Connecting certain indexes, this paper intends to discern laws governing the copper production phase. Under the circumstances, with lower grade copper ore, how does the U.S. extract copper from ore below the commercial grade? How does the U.S. adjust the structure of production? How does the U.S. use primary and secondary copper resources? These regulations provide a reference and enlightenment for a newly industrialized country.

2. Literature review

Substance flow analysis (SFA) is a systematic assessment of stocks and flows of noxious or specific elements within a predefined temporal and spatial system boundary. The SFA originates from the material flow analysis (MFA) (Brunner and Rechberger, 2004). Both the MFA and SFA obey the law of mass conservation. For the SFA, the general principle, mass conservation, aids in tracking the input to, output from, stock of and loss to the environment of one substance through its life cycles (Spatari et al., 2002; Brunner and Rechberger, 2004). The MFA and SFA frameworks have been gradually presented in subsequent studies (Baccini and Brunner, 2001; European Communities, 2001). Further, many studies have been performed in the last few decades because people are more concerned with environmental problems and sustainable development. Guinée et al. (1999) applied an SFA to analyze copper, cadmium, lead and zinc in the Netherlands. They quantified the risks from emission and accumulation of these metals in the Netherlands. Next, Van der Voet et al. (2000) used the models to track the fate, transport, and accumulation of cadmium, zinc, copper and plumbum in Netherlands and show a relationship between environmental problems and metal extraction and use. Spatari et al. (2002) provided a detailed analysis of the European copper cycle from a stocks and flows (STAF) perspective through the entire copper life cycle. Graedel and colleagues quantified copper flow in the U.S. economy. Kapur et al. (2003) studied the contemporary copper cycle in Asia using an SFA framework and the STAF model and found that copper accumulation and use is 3 Tg Cu/year. Further, the secondary copper recovery rate is low compared with western developed countries, except Japan. Yue and Lu (2005a,b) and Guo and Song (2008) applied an SFA and the STAF model to analyze copper conditions in China, including the cooper self-sufficient and scrap-use rates, ore index, copper resource efficiency and scrap index.

Industrialization requires large quantities of metal, exhaustible resources. Thus, people gradually realized the importance of metal scrap and began to pay attention to recycling metal scrap for sustainable development. Melo (1999) categorized and provided probabilistic representations for the service life of end-of-life aluminum products. The author then estimated the increase in scrap in Germany based on the normal model, Weibull model, beta model and the new statistical model yield, which are better than the fixed lifetime model, which can aid in providing valuable decision making for both primary and secondary industries. Jackson et al. (2007) applied the Weibull and lognormal model to estimate the annual potential scrap generated based on iron and steel production and consumption in the UK. This paper revealed the annual loss or accumulation of scrap through a comparison with the model of scrap generated. Park et al. (2011) calculated the annual steel scrap generated based on the Weibull distribution model as well as a steady increase in scrap generation and provided a scenario analysis for different recycling rates in each iron-maintaining product group. The results revealed a sufficient supply for scrap demand if the recycling rate for iron-containing product groups increases. Based on Park's research, Wang et al. (2013) produced an SFA for zinc in China.

The previous studies provide two important contribution. First, they analyze material or a specific element from a global, continental or national level. Second, they concentrate on social stock and annual potential scrap generated for metals based on production and use. The studies mainly analyzed substances from a macroscopic perspective and studied the latter two stages (use and waste management) using an SFA framework. Graedel et al. (2002) discussed characterizing anthropogenic copper cycle, including mining and processing, fabrication, use and end of life, which contributes to understanding the relevant processes and technology throughout the copper life cycle. Gordon (2002) provided detailed research on copper residues throughout a copper technological cycle. The study involved a detailed analysis of the production stage and aided in understanding the general conditions at the production stage, which greatly aids our research. However, the study only emphasized the technologies and did not concentrate on the development of copper in mature, developed countries. Thus, this paper emphasizes SFA for copper in the U.S. within the production boundary to discern laws that provide a reference to newly industrialized countries.

3. Methodology and data

3.1. System boundary for the copper cycle

Fig. 1 shows the system for the copper life cycle, where the stocks and flows of each stage are clearly presented. The dashed

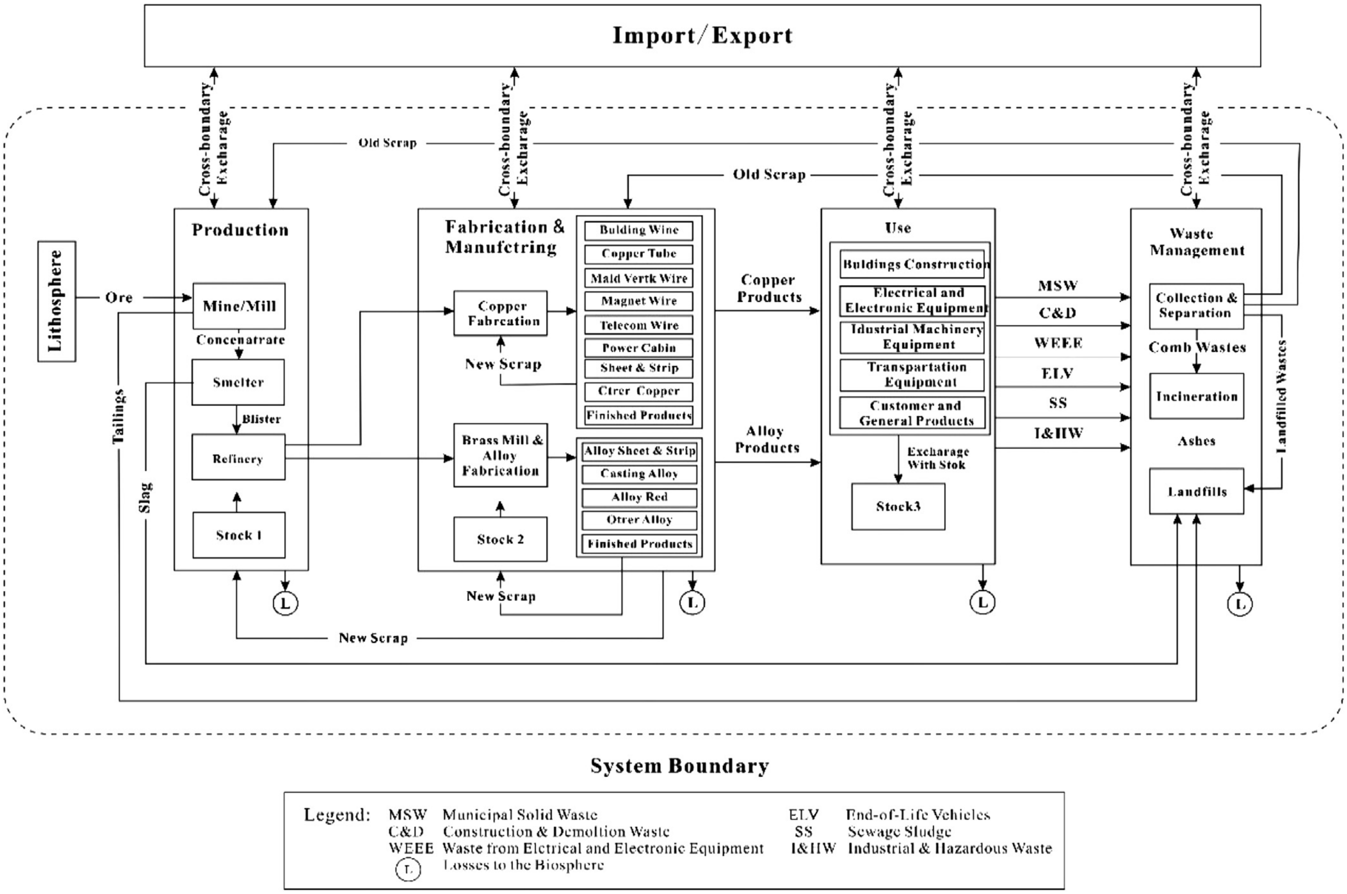

Fig. 1. System boundary for the copper cycle (Graedel et al., 2002). The use stage in this figure is slightly altered in this paper.

line in Fig. 1 indicates the system boundary for the SFA. Processes within the system boundary occur in the domestic environment. Foreign trade out of the boundary satisfies the gap between supply and demand. The SFA is composed of four main stages: production, fabrication and manufacture, use and waste management. These main stages include several sub-processes and are related. Due to conservation of mass, the output from one stage is the input for the subsequent stage.

The production stage includes the process where copper ore is mined from the lithosphere, and copper is extracted through metallurgical technology. Fabrication and manufacture include two components. The first component is fabrication of copper and alloy semis; the second component is manufacture of intermediate commodities and copper-finished products (Spatari et al., 2002). At the use stage, copper products from the fabrication and manufacture stage are used as products or embedded into assembled products and are mainly used in five fields, including building construction, electric and electronical equipment, industrial equipment, transportation equipment and other uses (Yue and Lu, 2009). Next, copper-containing products accumulate in society, and retired copper products are sent into the waste management system. Metal scrap within waste flow includes municipal solid waste (MSW), construction and demolition waste (C&D), waste from electrical and electronic equipment (WEEE), end-of-life-vehicles (EOLV), sewage sludge (SS), industrial waste (IW) and hazardous waste (HW) (Spatari et al., 2002). The copper scrap flow is routed into waste management subsystems, such as recovery, landfill, incineration, and loss to the environment (Bertram et al., 2002). Copper recovery (scrap) is routed through two processes. First, scrap can be processed to generate refined copper in the production stage and composes a portion of the refinery scrap (subsequent discussion will illustrate), and, second, scrap can be directly reused in the fabrication and manufacture stage.

3.2. Copper production process system boundary

SFA can provide a systematic analysis of the copper cycle from a macroscopic perspective. Certain hidden problems in one stage may be neglected (e.g., the structure and trend of refined copper production). Because a general SFA is based on the all of the conditions related to copper flow at each stage, it is vital to analyze copper in the production stage. Diverse types of copper minerals require different types of extractive metallurgy. For different types of copper extractive metallurgy technology, the material consumed and pollution problems during processing also differ. This paper focuses on copper in the U.S. and emphasizes the copper stocks and flows (STAF) within the production boundary in the SFA framework. This study was performed using the production stage system boundary, and the sub-processes are detailed in Fig. 2.

Mining and milling are the initial production stage processes that provide material for subsequent processes. Currently, copper extractive metallurgy is mainly divided into two methods: conventional extractive metallurgy and a solvent-extraction electrowinning (SX–EW) process. The output of electro-refining and electrowinning shown in Fig. 2 is for the primary production of refined copper. In fact, secondary production of refined copper is generated from scrap. The scrap delivered to produce refined copper is also referred to as refinery scrap. Refinery scrap is composed of new scrap from the fabrication and manufacture stage as well as old scrap from waste management. The sub-processes are elaborated upon in subsequent discussions in detail.

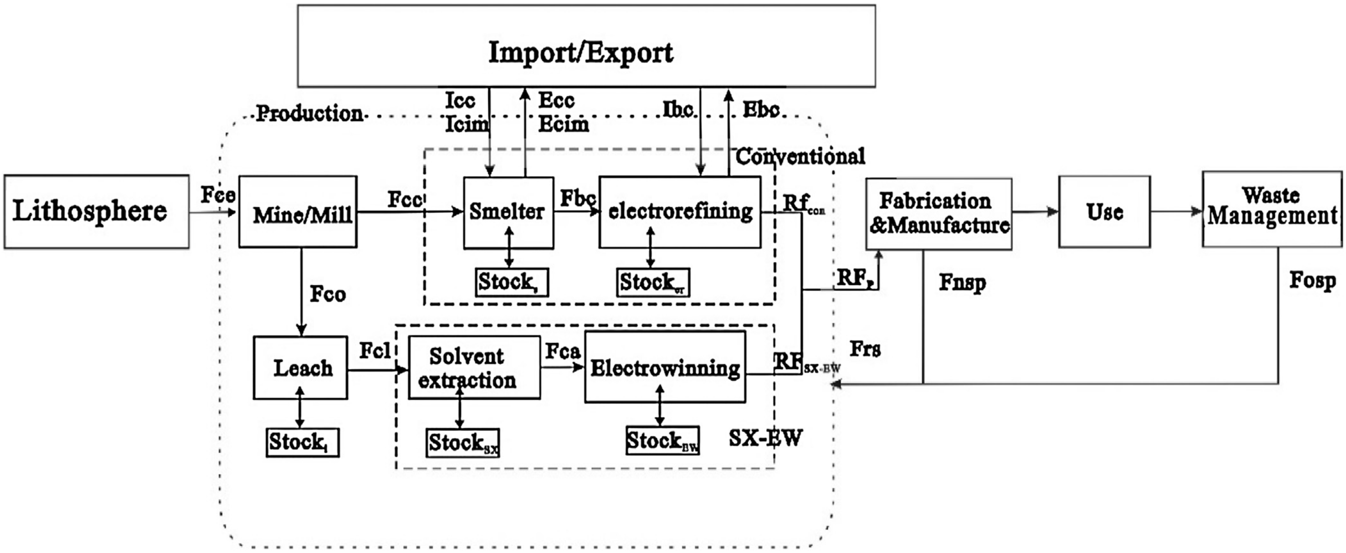

Fig. 2. The copper production process system boundary.

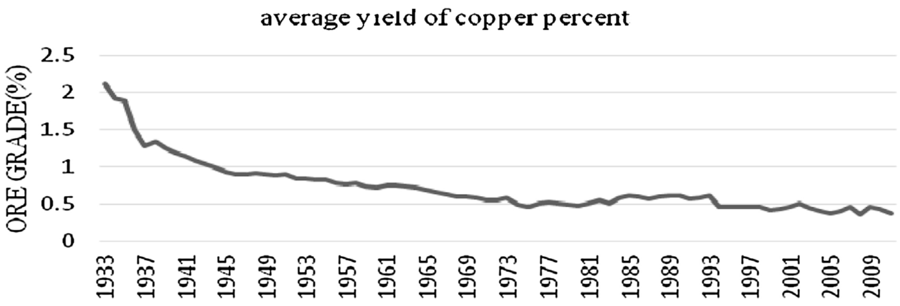

Fig. 3. Grade of copper ore (%) mined in the U.S. from 1933 to 2012

Data sources: USGS

3.3. Assumptions for the copper flow analyses

This paper includes five assumptions to better analyze the copper stocks and flows. (1) The inflow into a process is equal to the output and the change in stock. (2) To present the overall condition of copper stocks and flows in the US, this paper simplifies certain processes in Fig. 2 (e.g., some of the output from the leaching process, the copper leachate, is routed into the solvent-extraction process, and some is routed into precipitation to produce cement copper. However, the author cannot find data on cement copper flow, and it does not influence the analysis of this paper. Therefore, this paper omits the precipitation process). (3) This paper does not consider the loss to the environment (e.g., tailing from the milling process and slag from the smelter process) because the concentration of this paper is the condition of copper transformation flow in production stage sub-processes and the trend in refined copper production. Further, copper can be recovered from tailing and slag using certain processes (referring to Fig. 4), and data on copper recovered from the loss flow cannot be acquired. (4) The copper flows presented herein refer to copper content not gross weight. A special version of this paper will be provided to represent gross weight.

3.4. Data acquisition and calculation

This paper uses the substance flow analysis (SFA) method to provide a visual display of the copper life cycle in the United States from 1974 to 2012. The SFA provides a framework for tracking copper flow during the production stage. However, data from the mineral yearbook of USGS (www.usgs.gov) does not obey the conservation law fully in the SFA framework, which may be due to the statistic absence of in-process material stock. It is difficult to compile data on stock from different processes. Thus, this paper uses the stocks and flows (STAF) model to reconcile data to make up for the deficiency in statistics on stocks during the processes. We refer to stock and flow calculations (Zhang et al., 2014; Spatari et al., 2005; Wang et al., 2015).

The substance flow analysis (SFA) is based on mass conservation, which means that the inflow into a process is equal to the output and the change in stock. Each process calculation uses Eq. (1) to calculate the copper flow.

$$\text{Stock}_i = \sum_i F_{\text{input}} - \sum_i F_{\text{output}} \quad (1)$$

Eq. (1) expresses the basic copper flow within the process or stage. F designates the copper flow into and out of a process or stage. i represents the different copper cycle processes. $\sum F_{\text{input}}$ designates all input copper flow (including import and domestic production as the previous process) into the process. $\sum F_{\text{output}}$ designates all output copper flow (including export and copper production in many forms). Stock$_i$ designates the copper stocks (which can take many copper forms) in the copper cycle process.

The data used in this paper were generated prior to adoption of the official USGS statistics. The data that were not documented by official statistics were calculated by combining the current data and Eq. (1). Table 1 shows the data sources and corresponding

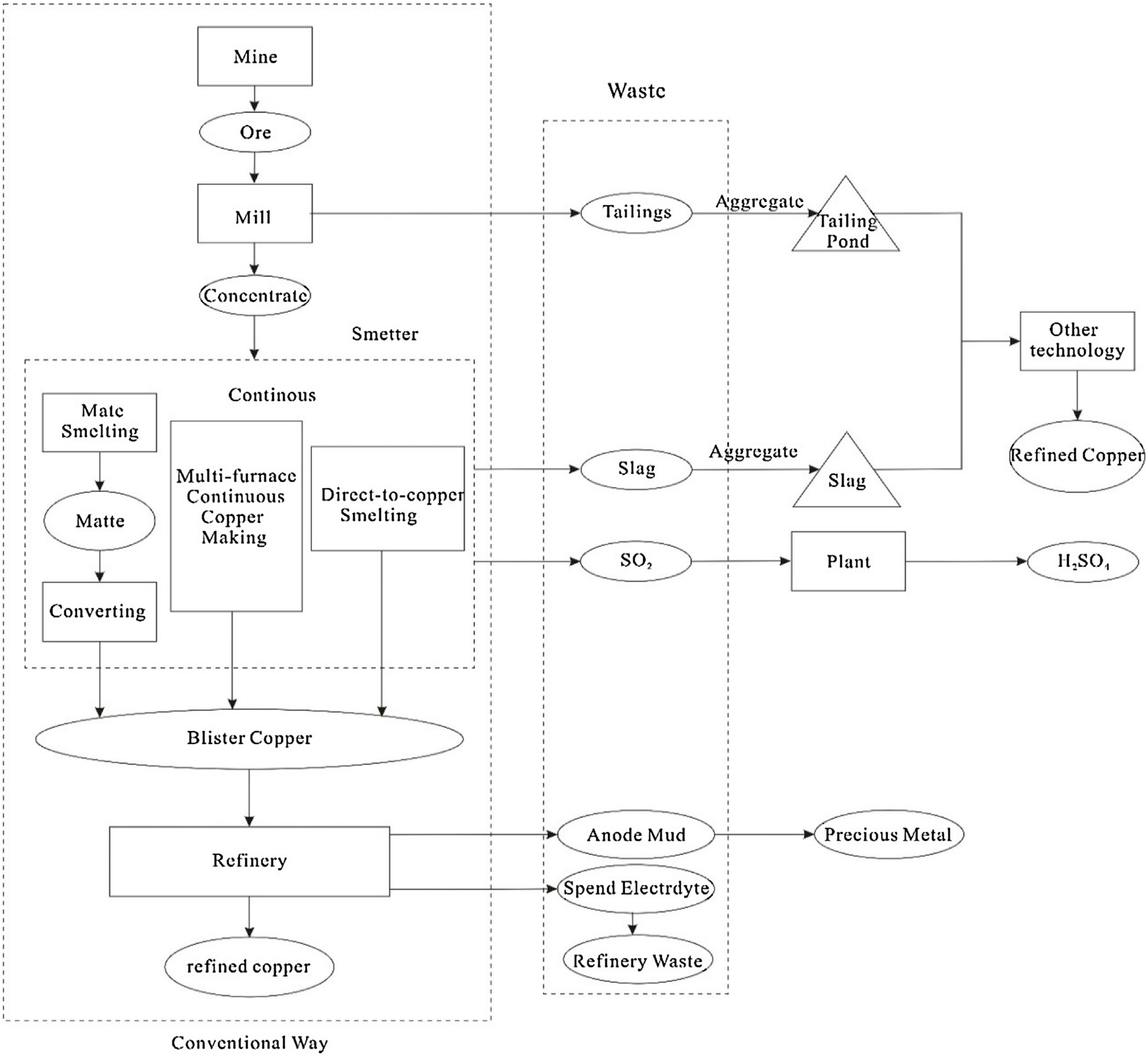

Fig. 4. Copper flow from a mine through conventional extractive metallurgy. Refer to Davenport et al. (2002); certain adjustments were used for this paper.

calculations for copper stocks and flows in Fig. 2. Using the SFA method and STAF model, the source, pathway and intermediate and final sinks for copper are clearly demonstrated for the production stage sub-process.

3.5. Index definitions

3.5.1. The domestic primary copper ore index

The domestic primary copper ore index measures the ratio of primary copper ore routed into the total production (including primary and secondary), and P_p is defined as follows:

$$P_p = \frac{F_{ce}}{(RF_p + F_{rs})} \quad (2)$$

where F_{ce} is domestic copper ore exploitation, RF_p is primary refined copper, and F_{rs} is scrap (including new scrap from the fabrication & manufacture phase and old scrap from the waste management phase), which is also referred to as refinery scrap.

3.5.2. The refinery scrap index

The refinery scrap index is the criterion used to measure how dependent a scrap resource is in the production stage. A larger P_s indicates that more scrap is necessary for the production stage; a lower P_s value indicates that less scrap is recovered in the production stage. The refined scrap index is defined as follows:

$$P_s = \frac{F_{rs}}{(RF_p + F_{rs})} \quad (3)$$

3.5.3. The SX–EW index

For the SX–EW index (solvent extraction–electrowinning), P_{sx-ew} is the criterion used to measure the proportion of refined copper from the SX–EW process. A larger P_{sx-ew} indicates that more refined copper is extracted from the SX–EW process in the refinery. The SX–EW P_{sx-ew} index is defined as follows:

$$P_{sx-ew} = \frac{RF_{sx-ew}}{(RF_p + F_{rs})} \quad (4)$$

Table 1
Stocks and flows of the copper cycle, assumptions and data sources.

Process	Flow	Assumptions and data sources	Calculation equation
Mine	F_{ce}: copper exploitation, current year	Based on statistics	
	F_{co}: copper core mined with low copper content	Based on statistics	
Mill	F_{cc}: copper concentrate through milling	Based on statistics	
Smelter	F_{bc}: blister copper	Based on statistics	
	Stock_s: stock change in the smelter process	Based on calculation	$\text{Stock}_s = F_{bc} + E_{cc} + E_{im} - I_{cc} - I_{cim} - F_{cc}$
	I/E_{cc}: imported or exported copper concentrate	Based on statistics	
	I/E_{im}: imported or exported in-process materials needed in smelter	Based on statistics	
Leach	F_c: copper ore into a leaching process	Based on statistics	
	F_{cl}: copper leachate		
	Stock_l: stock change of the leach process	Based on mass balance	$\text{Stock}_l = F_{cl} - F_c$
Solvent-extraction	F_{ca}: copper-loaded aqueous	Based on mass balance	$F_{ca} = F_c$
Electrowinning	$\text{RF}_{\text{SX–EW:}}$ primary refined copper produced through SX–EW technology	Based on statistics	
	Stock_{EW}: stock change from electrowinning	Based on mass balance	$\text{Stock}_{\text{EW}} = \text{RF}_{\text{SX–EW}} - F_{ca}$
Electrorefining	$\text{RF}_{\text{con:}}$ primary refined copper produced through conventional extractive metallurgy	Based on statistics	
	Stocke_r: stock change through electro-refining	Based on mass balance	$\text{Stocke}_r = \text{RF}_{\text{con}} + E_{bc} - F_{bc} - I_{bc}$
	$I/E_{\text{bc:}}$ imported or exported blister copper	Based on statistics	
	RF_p: primary refined copper production	Based on mass balance	$\text{RF}_p = \text{RF}_{\text{con}} + \text{RF}_{\text{SXE–W}}$
Fabrication and Manufacture	F_{nsp}: new scrap from the fabrication and manufacture stage into the production stage to produce refined copper	A portion of refinery scrap Based on statistics	
Waste management	F_{osp}: old scrap from waste management into the production stage to produce refined copper	A portion of refinery scrap Based on statistics	
	F_{rs}: refinery scrap	Refined copper produced from new and old scrap	$F_{rs} = F_{nsp} + F_{osp}$

where $P_{\text{sx–ew}}$ is the primary refined copper from the solvent extraction–electrowinning process.

3.5.4. The index of net imported refined copper

The index of net imported refined copper (NIRF) indicates the net imported refined copper that accounts for the primary and secondary refined copper from the production phase. This paper uses Eq. (5) to define NIRF:

$$\text{NIRF} = \frac{I_{rc} - E_{rc}}{\text{RF}_p + F_{rs}} \times 100\% \tag{5}$$

where I_{rc} is imported refined copper for the current year, and E_{rc} is exported refined copper for the current year.

4. Processing copper in the production stage

Copper flow in the production stage within the U.S. spatial boundary is composed of two components: mine production copper ore and extractive metallurgy of copper. Copper is found in nature in many forms, including cuprite, covellite, chalcopyrite, malachite, and native copper. Different types of copper-containing minerals feature diverse characteristics, which results in many differences. The first is different technologies used for mining production and extractive metallurgy, the second is different energy and economic consumption, and the third is different environmental pollution problems caused by the production processes.

Referring to Davenport et al. (2002), this paper classifies copper ore as three main forms of minerals as shown in Table 2.

4.1. Mining

Copper ores are composed of a mixture of copper-bearing minerals and the companion gangue (such as quartz, limestone and calcite). Copper ore is mined through underground and open-pit mining. Underground mining that is generally limited to rich ores is relatively expensive. Open-pit mining is employed to extract minerals that are low-grade and relatively near the surface (Vin Calcutt, 2001). Open-pit mining supplants underground mining due to technological advances (Graedel et al., 2002). Fig. 3 shows that the grade of copper ore decreases as people exploit the copper ore. The grade of copper ore is approximately 0.5% after the 1960s and even falls below 0.5% after the 1990s. The American grade of copper ore is lower than the lowest copper deposit levels, which are generally in excess of 0.5% and preferably over 2%, for commercial exploitation (Vin Calcutt, 2001). However, leaner ores can be exploited due to many technological advances in the production stage processes (which will be introduced in a subsequent article).

Table 2
Copper minerals.

Species	Mineral	Main composition	Theoretical copper content (%)
Sulfide form	Chalcopyrite	$CuFeS_2$	34.6
	Bornite	Cu_5FeS_4	63.3
	Chalcocite	Cu_2S	79.9
	Covelite	CuS	66.5
Oxide form	Cuprite	Cu_2O	88.5
	Tenorite	CuO	79.9
	Malachite	$CuCO_3{\cdot}Cu(OH)_2$	57.5
	Azurite	$2CuCO_3{\cdot}Cu(OH)_2$	55.3
	Chrysocolla	$CuO{\cdot}SiO_2{\cdot}2H_2O$	36.2
	Connellite	$Cu_2Cl(OH)_3$	59.5
Other	Native copper	Cu	100

4.2. Milling

Milling is necessary for copper ore that will be sent to a smelter because the copper content (0.5–2%) is too low to satisfy the smelter demand (Davenport et al., 2002). Low-grade ores consist of many gangues that require much energy and a large-capacity furnace. However, hydrometallurgical processes (a subsequent paper will illustrate) require almost no milling, but they extract copper from crushing ores.

The milling processes produce concentrates that generally contain approximately 30% copper, but the copper content ranges from 20 to 40 (International Copper Study Group, 2012) when the metal-bearing mineral is separated from ores extracted from the lithosphere. The dressing mill is often close to the mine to reduce the cost of hauling barren rock. Copper ores will be crushed and ground followed by froth flotation (mainly) as well as occasional assistance from other equipment or technologies. Froth flotation separates copper minerals; the barren rock then liberates the copper concentrate and tailings with residual leaner copper minerals. Mill operators store copper tailings to construct tailing-pond dams (Davenport et al., 2002; Hancock and Pons, 1999) that aggregate copper-bearing tails and can extract copper through new metallurgical technologies, such as solvent extraction electrowinning (SX–EW). In U.S., 684 metric tons of copper was extracted by leaching tailings in 2003.

4.3. Conventional copper extraction

Conventional copper extraction is a pyrometallurgical process that includes smelting and refining. Copper concentrate from the milling process is used in the smelter process. Smelting can be divided into three general types of smelting processes: direct smelting, a two-stage process and the Misubishi continuous smelting method (the best copper smelting process). Further, bath smelting and flash smelting includes matte smelting and smelting by flown.

Copper concentrates milled from copper minerals in sulfide form (such as Chalcocite, Chalcopyrite, Covellite) are heated to 1200–1300 centigrade to separate the dioxide from the copper sulfide concentrate in the reverberatory furnaces. The process is referred to as matte smelting, which has been used as a standard method for 75 years, wherein matte (mainly Cu_2S) and slag with the approximate composition $FeO{\cdot}SiO_2$ are produced (Gordon, 2002). Molten matte from the reverberatory furnaces is converted to blister copper (containing 98% Cu) and SO_2 gas by flowing with air in the converter (Hayward, 1952; Gordon, 2002).

The thermal energy from the oxidation reactions will not be utilized, and the SO_2 gas released from the furnace is too dilute to efficiently produce sulfuric acid. Certain developed countries recover the stack gases to mitigate the environmental problem (acid rain) caused by the SO_2 emission gas through technological improvements (Graedel et al., 2002). Due to the energy consumption and environmental regulation limitations, copper producers have gradually adopted new technologies, including Misubishi, Noranda, El Teniente, Outokrumpu, INCO, Isasmelt, Ausmelt, and shaft furnace techniques (George et al., 1999).

Blister copper from a smelting process is transported to a refinery. A two-stage process will aid in producing cathodes containing over 99.99% of copper. At first, the blister is fire-refined to reduce the oxygen and sulfur from the previous process to prevent a rough anode surface. The molten copper output from the process is then cast into anodes for the second electro-refining stage. The outcome of an electrolytic refined process is a desired purity copper product that is referred to as cathode and precious metal from the anode mud. Table 3 shows the anode mud composition at the Kennecott Utah refinery (Dutrizac et al., 1999). American porphyry copper deposits feature a mixture of precious metals, such as molybdenum, rhenium, gold and silver. In the U.S., certain companies can extract precious metals from old or dumped mines, which render the mine profitable for exploiting low grade copper ore at levels even below 0.5% (The Chinese Society for Metals, 1978).

Table 3
Percentage of anode mud composition (%) at the Kennecott Utah refinery.

Cu	Ag	Au	Se	Te	As	Sb	Bi	Fe	Ni
20	5	0.5	5	1	5	1	3	0.25	0.05

4.4. Solvent extraction–electrowinning

The solvent extraction–electrowinning process (SX–EW) is a hydrometallurgical process that extracts copper from the mainly low-grade oxide ores and certain sulfide ores as an alternative to conventional extractive metallurgy. The SX–EW process was used at the Bluebird mine in Arizona in 1968 on a large scale and greatly increased the copper extraction efficiency (Dresher, 2001). The technology was adopted at mines in Arizona, Chile, and Africa in the 1970s and significantly improved through technological advances in copper extraction in the 1980s (Arbiter and Fletcher, 1994).

As Fig. 5 shows, the SX–EW process includes two main stages: the solvent extraction (SX) and electrowinning (EW) stages. At the SX stage, oxidized minerals (such as azurite, brochantite, chrysocolla and cuprite), residual copper in old mine dumps, tailings ponds from milling and sulfide minerals are leached in a sulfuric acid aqueous environment. However, a small portion of the sulfide is extracted using a new technology referred to as bacterial leaching. In addition, copper can be extracted from an ore body through an in situ leach, which greatly reduces the cost of transporting and removing valuable materials from the waste materials that otherwise would have been regarded as an environmental contaminant (Dresher, 2001). The leachate from the leaching process contains copper ion extracted from copper-bearing materials in an aqueous environment, which leaves behind most impurities. The copper-bearing aqueous phase is followed by the electrowinning stage (EW). Electrolysis of leachate converts copper ion to a cathode copper, which is the same as the refined copper from the electro-refining route. Thus, cathode copper both from conventional extractive metallurgy and SX–EW is well received by the market.

In the U.S., copper is considered a toxic material released into the environment. However, such environmental contaminants from copper mine dumps and flotation tailings are recycled as a copper resource component through the SX–EW process. Further, the SX–EW process reduces the SO_2 gas emission that cause acid rain if conventional means of copper extraction from sulfide ores are used, which is significant for the environment. The energy requirement for SX–EW depends on the origin of the copper-bearing materials leached and the particular conditions surrounding the installation. An estimate of the energy consumed from the SX–EW process is from 15 MJ/kg (from heap or dump solvent extraction) to 36 MJ/kg (from mined and crushed ores) compared with 65 MJ/kg from conventional processes. In the U.S., the energy consumed from SX–EW may vary due to the pumping cost of pregnant liquor (Dresher, 2001).

Compared with conventional metallurgy extraction means, the SX–EW process requires low capital investment, and a small-scale operation can operate economically, which may increase the probability of exploiting small ore bodies.

Generally, compared with conventional processes, the SX–EW process has many advantages, as mentioned previously (environmentally friendly, extractive metallurgy efficiency, low energy consumption, low investment, etc.); thus, this process has been widely adopted and used worldwide(Moats and Free, 2007).

5. Results and discussion

This paper used data on copper from the USGS and connects the SFA framework to present the stocks and flows of copper in the U.S. throughout its entire life cycle (which is especially complicated in the production stage). The following discussion is on the stocks and flows of American copper in 1974, 1986, 1998, 2010 and 2012. Looking through the statistics from the mineral yearbook from 1933 to 2013, we found that the data classification and

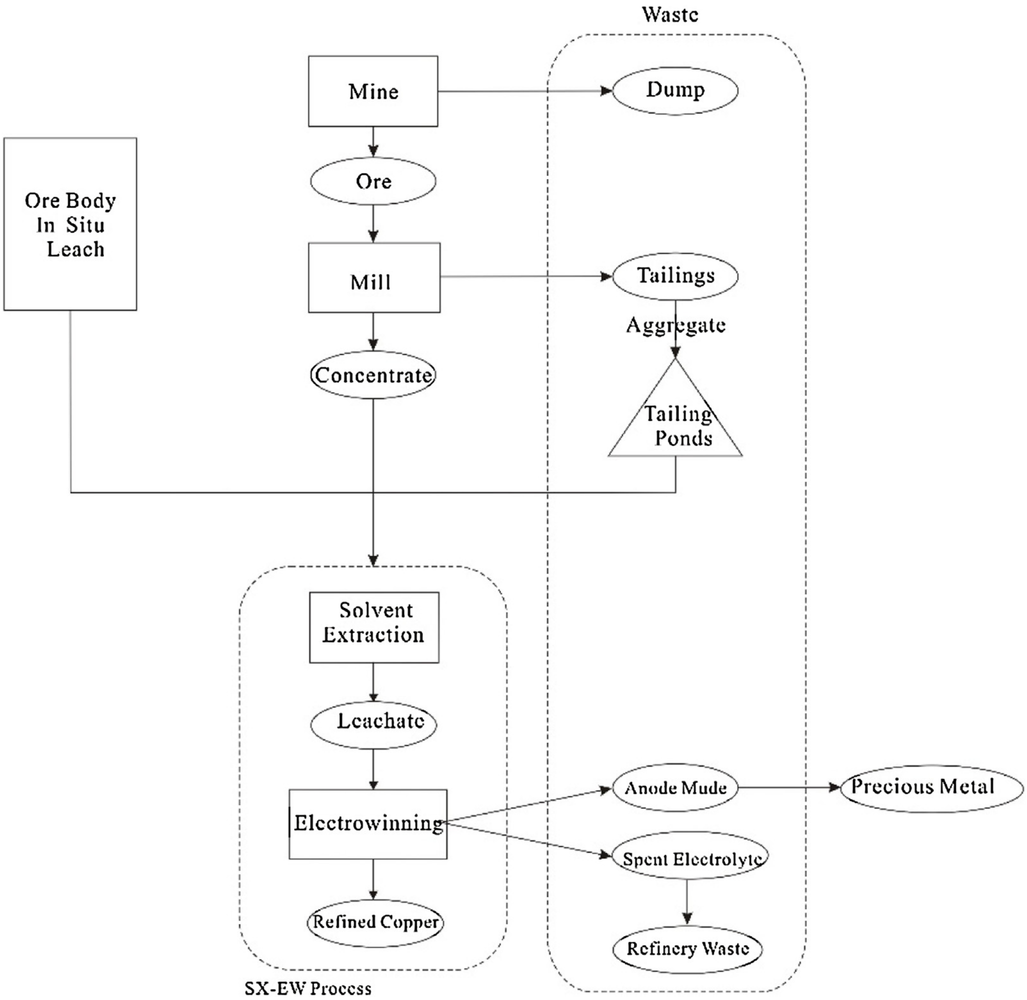

Fig. 5. Copper flow from a mine through the SX–EW process. Refer to Gordon (2002); certain adjustments were used for this paper.

processing differ greatly among different periods. Thus, this paper makes certain adjustments to unify the classifications. This paper only considers refined copper documented in the mineral yearbook of the USGS and does not consider other forms of refined copper (detailed information can be found in the mineral yearbook of the USGS before 1980).

The next section will involve many acronyms for copper flow and indexes. These acronyms are introduced in Table 4.

5.1. An SFA of copper in 2012

Fig. 6 shows the copper stocks and flows for the U.S. at the production stage in 2012. From the picture, the source, destination, and numeral change in copper flow is clear. In 2012, American mine production was 1170 Gg/year, of which 699 Gg/year ores were concentrated, and 471 Gg/year ores were extracted through leaching. Some of the copper concentrate was then fed to a smelter to produce 485 Gg/year blister copper with 98% purity. The blister copper was not sufficiently pure to satisfy the market requirements. Thus, the blister copper was delivered to the refinery to produce pure refined copper with 99.9% copper (also referred to as cathode) through electro-refined means. The electrolytic copper produced was 491 Gg/year, and the electrowinning copper produced was 471 Gg/year. One country would not fully rely on domestic copper ore for the production process.

Copper-containing materials necessary to the production stage are traded for the smelter and electro-refining processes. Trade for the smelter process includes concentrate and in-process materials (as matte, ash, and precipitates). Further, trade for the electro-refining process includes blister copper. Thus, in 2012, the concentrate and in-process materials imported for the smelter process comprised 6.29 Gg/year and 1.5 Gg/year, respectively. Further, the exported ore and in-process materials composed 301 Gg/year and 35.8 Gg/year, respectively. The blister copper imported for the electro-refining process totaled 0.554 Gg/year, and the exported blister copper totaled 13.9 Gg/year. The refinery scrap recovered in the production stage to produce refined copper totaled 39.5 Gg/year. In 2012, the refinery scrap was composed of two components: one component was 17.9 Gg/year of new scrap from manufacture processing, and the other component was 21.8 Gg/year old scrap from the waste management stage.

5.2. The SFA for the United States in 1974, 1986, 1998, and 2010 compared

The U.S. copper cycles from 1974 to 2010 are shown together in Fig. 7. These figures clearly illustrate the conditions of the copper stocks and flows for each production stage sub-process. To analyze these conditions, a subsequent article may calculate the ratios, such as the P_p, P_s, and P_{sx-ew}. Table 4 shows the results for the three indexes P_p, P_s, and P_{sx-ew} in 1974, 1986, 1998, 2010, and 2012.

The ratio of the domestic primary ore P_p rose by degree, which indicates that the proportion of domestic ore increased, and the

Table 4
Acronyms in the results.

Flow	Acronym	1974	1986	1998	2010	2012
Refinery scrap	RS	380.163	405.944	349.000	37.700	39.500
Domestic copper ore	DPO	1448.784	1147.277	1860.000	1110.000	1170.000
Primary refined copper	PRC	1522.106	1073.21	2137	1057	962
Electrowon	EW	21.017	125.352	609	430	471
Index (%)	Acronym	1974	1986	1998	2010	2012
Index of domestic ore	Pp	76.16	77.56	74.81	101.40	116.82
Index of refinery scrap	PS	19.98	27.44	14.05	3.44	3.94
Index of SX–EW	PSX–EW	1.10	8.47	24.49	39.28	47.03
Index of net imported refined copper	NIRF	9.97	33.1	24.01	48.11	47.03

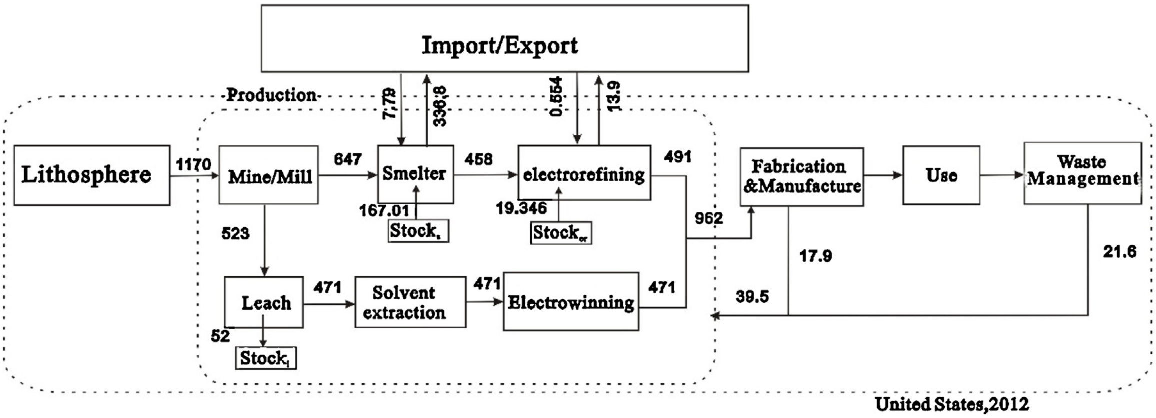

Fig. 6. The U.S. copper cycle in 2012. All units are in Gg/year (thousand metric ton/year).

domestic copper ore can fully satisfy refined copper production after 2010. Next, the P_p for 2012 was greater than 100% because a large quantity of copper material (including ore, in-process material and blister copper) was exported through foreign trade, and only 39.5 Gg/year refinery scrap was recovered in the refinery at the production stage.

The refinery scrap index P_s decreased by degree from 19.96% in 1974 to 3.94% in 2012. The decrease was due to three phenomena. First, the refinery scrap production scale decreased under strict environmental regulations (Jolly, 2012). Second, the recycling rate for new scrap in fabrication and manufacture gradually increased due to advancements in technology and equipment. Further, more new scrap was directly reused at the fabrication and manufacture stage rather than delivered to a smelter or refinery. Third, the waste management stage is better controlled than before. On the one hand, the old scrap was classified into diverse types of scrap, which was then directly reused at the fabrication and manufacture stage. On the other hand, the scrap remaining after classification (including low copper-content scrap and scrap that was only slightly disassembled from retired copper-bearing products) was delivered to other countries through foreign trade (Goonan, 2010).

The SX–EW $P_{\text{sx-ew}}$ index exhibited a clear increase from 1974 to 2012. The ratio increased by almost 42-fold. The variation trend shows the high speed of development for the SX–EW process and that refined copper is more dependent on the hydrometallurgical process than before. This trend is due to four phenomena. First, American low-grade copper ore is the main limitation. Mines produce low-grade copper ore that is not in excess of the critical point for commercial exploitation 0.05%. The low-grade copper ore cannot directly meet the conventional metallurgy requirements and must be concentrated through milling, which may consume energy. Second, the environmental regulations were tighter than before. Conventional metallurgy produces waste, such as SO_2 gas, tailings and slag. The waste released into the environment would cause many environmental problems. Compared with this scenario, in the SX–EW process, no SO_2 gas is emitted, and waste, such as tailings and dumps, can be recovered. Third, technological advances in the SX–EW process can be used to directly extract copper from low-grade oxidized materials, such as azurite, brochantite, chrysocolla, and cuprite, without concentration through floatation. Further, bacterial leaching, which is used in conjunction with the SX–EW process, can greatly improve the efficiency of extracting copper from sulfide minerals. Fourth, the SX–EW process, which is used in conjunction with smelting, accelerates the waste recycling process for conventional extractive metallurgy. The American sulfuric acid market is in a depression; thus, it is not profitable to recycle SO_2 gas from smelting to generate sulfuric acid. However, the SX stage requires a weak acid environment, which inspires copper producers to recycle waste to reduce costs and environmental pollution.

5.3. *Refined copper production*

Fig. 8 clearly shows the conditions for all refined copper production (including primary and secondary) from 1924 to 2011. Refined copper production from conventional processes and scrap has decreased, but production using electrowon means increased after 1968 and has held steady since 1998. All refined copper production gradually decreased after 1998. Connected with the previous analysis, the scale of primary and secondary copper production has clearly decreased from its peak in the 21st century. Primary copper production peaked in 1998 and then gradually declined. Refinery scrap production peaked at 515 Gg/year in 1980 and then fluctuated with to 450 Gg/year. After 2001, refinery scrap production decreased rapidly and has remained blow 50 Gg/year since 2005.

As Fig. 8 shows, primary refined copper production in the U.S. fully relied on conventional extractive metallurgy before 1970. The SX–EW process was not used on a large scale before 1968 and was

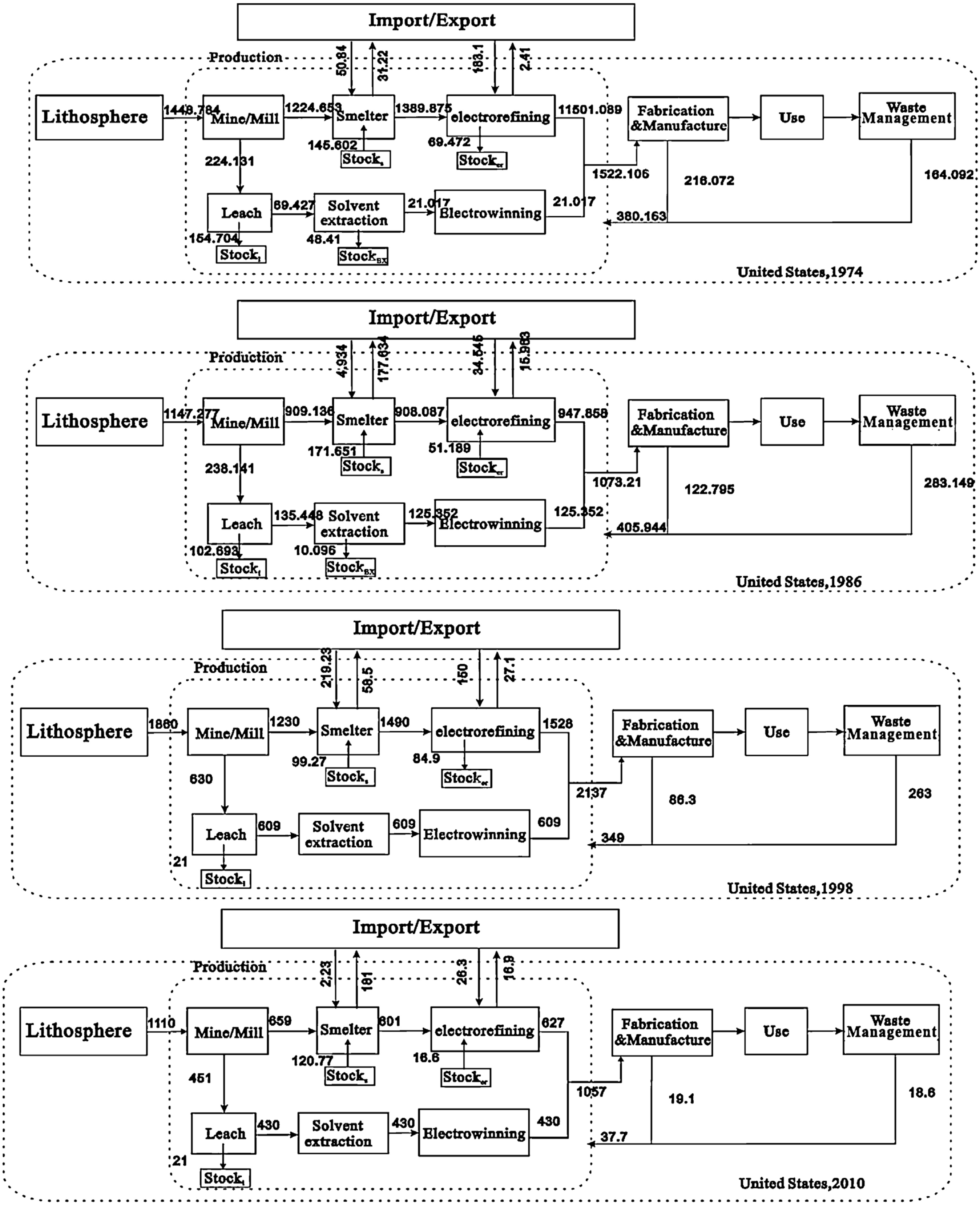

Fig. 7. The U.S. copper cycle from 1974 to 2010. All units are in Gg/year.

used to extract 609 Gg/year copper in 1998. The SX–EW production quantity was small before the 1980s; no more than 100,000 metric tons was produced, except in 1977. The SX–EW process produced approximately 100,000 metric tons of copper. Its production then greatly increased after 1990, peaked at 628,000 metric tons in 2001 and is stable at approximately 450,000 metric tons. Primary refined copper production peaked at 2,137,000 metric tons of copper in 1998.

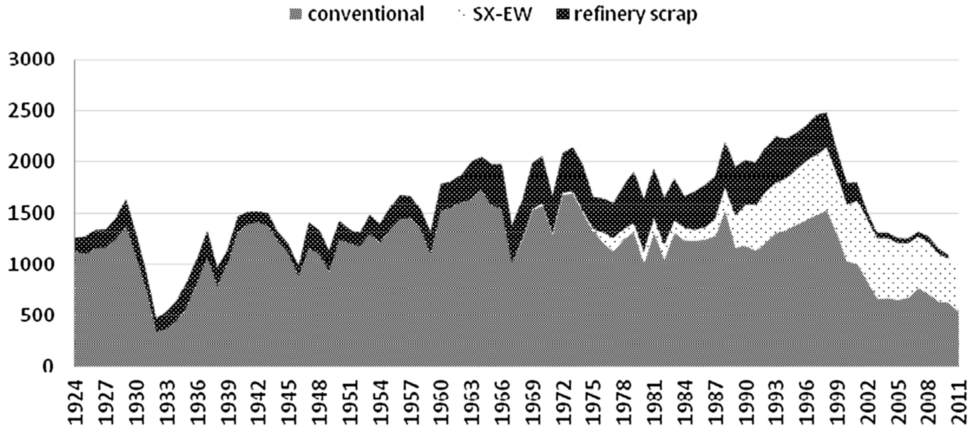

Fig. 8. Refined copper production in the U.S. from 1924 to 2012. All units are in Gg/year.

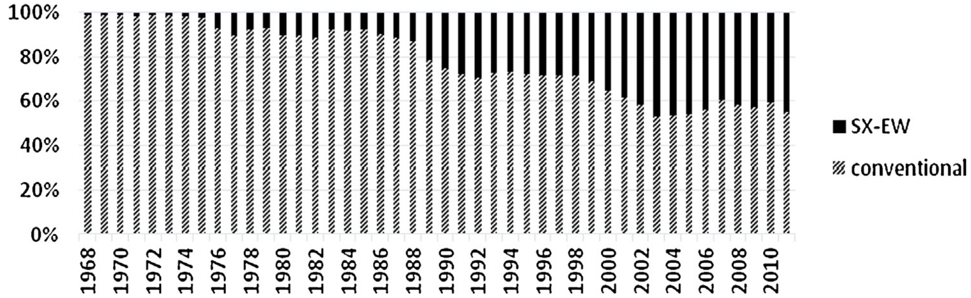

Fig. 9. The percentage of refined copper from two technologies from 1968 to 2010.

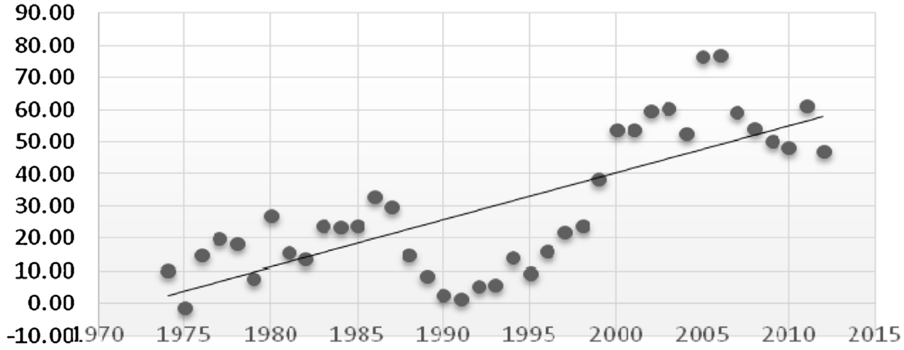

Fig. 10. The index of net imported refined copper (NIRF).

Consider intensive observations on primary production using the conventional and SX–EW processes. The percentage of primary copper produced from the two processes is shown in Fig. 9. The percentage from SX–EW is increasing and peaked at 47.17% in 2003; since then, it has remained at approximately 45%. The percentage trend clearly varied from less than 1% at its initial used to 45% at present. Combining Figs. 8 and 9, the data clearly show that the quantity of primary copper from SX–EW rose greatly before 2001 and gradually decreased after 2001. However, the percentage increased from 1968 to 2000, and has remained stable at approximately 45% in the 21st century.

The scale of refined copper generated at the production stage decreases, while consumption is increasing every year. Generally, the U.S. bridges the gap between consumption and production through the foreign trade. Further, the copper consumption in the fabrication and manufacture phase is not limited to refined copper but includes copper semi-manufactures, such as pipes, plates, bars, and wires. However, this paper emphasizes the production phase and does not consider the fabrication and manufacture phase.

The results calculated for the NIRF are shown in Fig. 10.

The NIRF is consistent with the M shape, which shows that the entire trend for NIRF has increased, except for during the nineties in the 20th century. The NIRF is less than 10% initially and increased to 55% with fluctuations. The decline in the ratio is due to two mathematical phenomena: one, the decrease in the net imported refined copper and, two, the increase in domestic refined copper production.

Certain crucial events occurred in the world during this period. A disruption in Africa, Canada, Mexico and Papua New Guinea constrained the world copper mine supply to a certain extent. Thus, the world copper supply was tight and inventories declined to partially offset the gap between supply and demand. The United States continued to expand copper mine production (Jolly and Edelstein, 1989).

In 1992, the United States expanded existing mines and initiated several leach operations. Further, domestic mine productivity decreased from 17.7 worker hours per ton in 1991 to 15.9 worker hours in 1992, which also contributed to the increase in copper mine production (Edelstein, 1992). The negotiation of trade agreements, such as The North American Free Trade Agreement and General Agreement on Tariffs and Trade, significantly influenced foreign trade. Only 58.325 Gg/year of refined copper was exported in 1988, while 263.217 Gg/year was exported in 2001 for the United States. Global copper demand decreased, and the main increase in copper consumption was from semi-fabrication plants in Asia and Europe (Jolly and Edelstein, 1989).

The NIRF ratio for 2005 and 2006 was much higher than for other years. The gap in domestic copper production was bridged by an increase in net imported refined copper. The net imported refined copper rose from 960,500 tons in 2005 to 689,000 tons in 2004, which is an increase of 39.48%. The refined copper imports accounted for 85.47% of unmanufactured copper imports in 2005. The conditions in 2006 were roughly the same as in 2005. The slight decline in NIRF after 2008 is likely due to the scale of net imported refined copper and domestic refined production, which decreases, and the net imported refined copper decreased faster than the domestic refined copper.

6. Conclusions

This paper introduces the contemporary copper cycle for the U.S. and describes sub-processes (including the mine, milling, smelter and refinery) within the production boundary in detail. Copper production is divided into two methods, conventional extractive metallurgy and the SX–EW process, which are based on copper production processing. Copper is extracted from high-grade copper ores, such as ores, through conventional extractive metallurgy. Further, for low-grade copper ores, such as oxidized ores and certain sulfides, tailings, and dumps, copper is extracted through the SX–EW process. Copper production using the SX–EW process is increasing due to its environmentally friendly aspects.

This paper emphasizes copper stocks and flows during the production and analyzes the copper conditions in 1974, 1986, 1998, 2010 and 2012. The calculated results show that the P_{p} and $P_{\mathrm{sx-ew}}$ increased, while the P_{s} decreased. The index (as P_{p}, P_{s} and $P_{\mathrm{sx-ew}}$) revealed that primary domestic refined copper has gradually become more dependent on the SX–EW process. Refined copper production from conventional extractive metallurgy decreased during this period, except for during the last decade in the 20th century.

The scale of refined copper production (including primary and secondary refined copper) has gradually decreased due to two phenomena. First, the source for primary copper has decreased; on one hand, domestic mine production decreased after 1998, and, on the other hand, a portion of the copper ores were exported through foreign trade. Second, the secondary copper flow into the U.S. copper production system (also referred to as refinery scrap) decreased (Jolly, 2012). In addition, the refinery scrap was below 50 Gg/year after 2001.

The net imported refined copper partially offsets the decreased in domestic refined copper production. The NIRF is consistent with an M shape. The general trend for the NIRF is ascendant, except for a special period. An interruption in the main copper supply country yields a tight copper market, which leads to an increase in domestic refined copper production.

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References

Arbiter, N., Fletcher, A.W., 1994. Copper hydrometallurgy evolution and milestones. Min. Eng. 46 (2), 118–123.

Baccini, P., Brunner, P.H., 2001. Metabolism of the Antroposphere. Springer Verlag, Berlin.

Bertram, M., Rechberger, H., Spatari, S., Graedel, T.E., 2002. The contemporary European copper cycle: waste management subsystem. Ecol. Econ. 42, 43–57.

Brunner, P.H., Rechberger, H., 2004. Practical Handbook of Material Flow Analysis. Lewis Publisher, Boca Raton, FL.

Copper Development Association Inc. (CDA), Jolly, J.L., available online http://www.copper.org/ 2012. The U.S. Copper-base Scrap Industry and Its By-products.

Davenport, W.G., King, M., Schlesinger, M., Biswas, A.K., 2002. Extractive Metallurgy of Copper, 4th ed. Pergmon, Oxford.

Dresher, W.H., 2001. How Hydrometallurgy and the SX/EW Process Made Copper the "Green" Metal. Copper Applications in Mining and Metallurgy, http://www.copper.org/publications/newsletters/innovations/2001/08/hydrometallurgy.html.

Dutrizac, I.E., Li, J., Ramachandran, V., 1999. Copper 99, vol. III, Electrorefining and Electrowinning of Copper. TMS, Warrendale.

Edelstein, D.L., Available at http://minerals.usgs.gov/minerals/pubs/commodity/copper/ 1992. Copper Mineral Yearbook (1988–1992).

European Communities, 2001. Economy-Wide Material Flow Accounts and Derived Indicators: a Methodological Guide. Office for Official publications of the European Communities, Luxembourg.

George, D.B., et al., 1999. Copper 99, vol. V. Smelter Operations and Advances. TMS, Warrendale.

Goonan, T.G., 2010. Copper Recycling in the United States in 2004, Available at http://pubs.usgs.gov/circ/circ1196x/.

GordonF R.B., 2002. Production resides in copper technological cycles. Resour. Conserv. Recycl. 36, 87–106.

Graedel, T.E., Bertram, M., Fuse, K., Gordon, R.B., Lifset, R., Rechberger, H., Spatrari, S., 2002. The contemporary European cycle: the characterization of technological copper cycles. Ecol. Econ. 42, 9–26.

Graedel, T., Van Beers, D., Betram, M., Fuse, K., Gordon, R., Gritsinin, A., Kapur, A., Klee, R., Lifset, R., Memon, L., 2004. Multilevel cycle of anthropogenic copper. Environ. Sci. Technol. 38 (4), 1242–1252.

Guinée, J.B., van den Bergh, J.C.J.M., Boelens, J., Frannje, P.J., Huppes, G., Kandelaars, P.P.A.A.H., Lexmond, T.M., Moolenaar, Olsthoorn, A.A., Udo de Haes, H.A., Verkuijlen, E., Van der Voet, E., 1999. Evaluation of risks of metal flows and accumulation in economy and environment. Ecol. Econ. 30, 47–65.

Guo, Xueyi, Song, Yu, 2008. Substance flow analysis of copper in China. Resour. Conserv. Recycl. 52, 874–882.

Hancock, B.A., Pons, M.R.L., 1999. Copper 99, vol. II. Mineral Processing. Environment, Health and Safety. TMS, Warrendale.

Hayward, C.R., 1952. An Outline of Metallurgical Practice, 3rd ed. Van Nostrand, New York.

International Copper Study Group, 2012. The World Copper Factbook, http://www.icsg.com/.

Jackson, T., Davis, J., Geyer, R., Ley, J., He, J., Clift, R., Kwan, A., Sansom, M., 2007. Time-dependent material flow analysis of iron and steel in the UK. Part 2. Scrap generation and recycling. Resour. Conserv. Recycl. 51, 118–140.

Jolly, J.L.W., Edelstein, D.L., 1989. Copper Mineral Yearbook (1985–1989), http://minerals.usgs.gov/minerals/pubs/commodity/copper/.

Kapur, A., Bertram, M., Spatari, S., Fuse, K., Graedel, T.E., 2003. The contemporary copper cycle of Asia. J. Mater. Cycles Waste Manag. 5 (2), 143–156.

Li, Mingzhao, 2010. Non-ferrous Metals Metallurgy Process. Chemical Industry Press, Beijing [in Chinese].

Melo, M.T., 1999. Statistical analysis of metal scrap generation: the case of aluminium in Germany. Resour. Conserv. Recycl. 26, 91–113.

Moats, M., Free, M., 2007. A bright future for copper electrowinning. J. Miner. Met. Mater. Soc. 59 (10), 34–36.

Park, J., Hong, S., Kim, I., et al., 2011. Dynamic material flow analysis of steel resources in Korea. Resour. Conserv. Recycl. 55 (4), 456–462.

Spatari, S., Bertram, M., Fuse, K., Graedel, T.E., Rechberger, H., 2002. The contemporary European copper cycle: 1 year stocks and flows. Ecol. Econ. 42 (1), 27–42.

Spatari, S., Bertram, M., Gordon Robert, B., Henderson, K., Graedel, T.E., 2005. Twentieth century copper stocks and flows in North America: a dynamic analysis. Ecol. Econ. 54 (1), 37–51.

The Chinese Society for Metals, 1978. The Metallurgical Industry Survey of Non-ferrous Metals. Press of Metallurgy Industry, Beijing.

Van der Voet, E., Guinée, J.B., Udo de Haes, H.A., 2000. Heavy Metals: a Problem Solved? Kluwer Academic Publishers, Dordrecht.

Vin Calcutt, 2001. Introduction to Copper: Mining and Extraction. Copper Application in Metallurgy of Copper and Copper Alloys, http://www.copper.org/publications/newsletters/innovations/2001/08/intro_mae.html.

Wang, Anjian, Yan, Lingyu, Chen, Qishen, Li, Jianwu, 2013. Dynamic material flow analysis of zinc resources in China. Resour. Conserv. Recycl. 75, 23–31.

Wang, M., Chen, W., Li, X., 2015. One Year Substance Flow Analysis of Copper Cycle in U.S. In: Proceedings of the Ninth International Conference on Management Science and Engineering Management, Springer Berlin Heidelberg, pp. 1265–1272.

Yue, Q., Lu, Z.W., Zhi, S.K., 2009. Copper cycle in China and its entropy analysis. Resour. Conserv. Recycl. 53 (2).

Yue, Qiang, Lu, Zhongwu, 2005a. An analysis of contemporary copper cycle in China – “STAF” method. China Resour. Compr. Util. 4, 6–21 (in Chinese).

Yue, Qiang, Lu, Zhongwu, 2005b. An analysis of contemporary copper cycle in China (II) – substance flow analysis with time factor of the life cycle of products. China Resour. Compr. Util. 5, 4–8 (in Chinese).

Zhang, L., Yang, J., Cai, Z., et al., 2014. Analysis of copper flows in China from 1975 to 2010. Sci. Total Environ. 478, 80–89.