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Global anthropogenic selenium cycles for 1940–2010

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ABSTRACT

Selenium plays an important role in emerging thin film solar energy technologies. As solar energy is expected to have a larger share in the world's future energy portfolio, the long-term availability of selenium becomes a potential concern, yet no global cycles have ever been generated. In this work, the global cycles, stocks, and flows of selenium are characterized for the entire time period 1940–2010 by using principles of material flow analysis (MFA). The cycles present information on the production, fabrication and manufacturing, use, and resource management stages during that period. The results of the analysis show that during 1940–2010 approximately 90 Gg of refined selenium was produced and entered into fabrication and manufacturing worldwide. 60 Gg of this amount (two-thirds!) was dissipated into the environment through end-uses such as chemicals, pigments, glass manufacturing, metallurgical additives, and fertilizer and feed additives. The in-use stock of selenium is estimated at 2.7 Gg as of 2010. Because of data limitations such as proprietary and withheld information, these figures represent informed estimates rather than exact values. Selenium can be recovered from end-of-life electrical and electronic equipment, while for other end-uses recycling is difficult or impossible. One of the ways to buttress supplies of selenium for future technologies would be to deploy recycling schemes for photovoltaics as well as other electronics applications.

1. Introduction

Selenium is an element with unique physical and chemical properties and diverse applications. One of its emerging end-uses as a semiconductor is in thin-film solar cells, namely copper indium (gallium) diselenide (CIS or CIGS). Because renewable energy is expected to play an important role in the world's future energy portfolio, the increasing use of selenium in an emerging renewable energy technology raises questions about the availability of selenium, among many other raw materials (Andersson, 2000; Bleiwas, 2010; Green, 2006; Moss et al., 2011).

Besides this emerging end-use, selenium is important to many other industrial sectors. Selenium acts as a decolorizer in glass manufacturing to remove the green tint imparted to glass by iron impurities. It is also used in pigments to color ceramics and glass. In the last decade, one of the growing end-uses of selenium has been in electrolytic manganese production, in which selenium is added to the electrolyte to increase the efficiency of the process. Selenium is also added to steels and lead-free alloys to improve their machining properties, and to low-antimony lead alloys in lead-acid batteries. Selenium is recognized as an essential micro-nutrient, and thus used as an additive to fertilizers for selenium deficient soils (IFA, 2011) and an additive to animal feed (FDA, 1994). High purity selenium is a semiconductor, was extensively used in photocopiers and rectifiers in the past, and is now being used in thin-film solar cells.

The future availability of materials can be explored by building anthropogenic material cycles through material flow analysis (MFA). The MFA of selenium can provide crucial information about how selenium is managed in the upstream stages of its life cycle, such as mining and refining, as well as the downstream stages, including use, discard, and end-of-life recycling. The concept of anthropogenic material cycles originated from the study of biogeochemical cycles of elements such as carbon, nitrogen, and sulfur. Similar to biogeochemical cycles, anthropogenic cycles follow and quantify the material flows and the stocks. The principal difference is that anthropogenic cycles focus only on the material flows induced by human activities to obtain the materials to be used in the economy.

MFA is a method that has been used to study cycles of elements of the periodic table such as iron (Wang et al., 2007), copper (Graedel et al., 2004), nickel (Reck et al., 2008), zinc (Graedel et al., 2005), tin (Izard and Müller, 2010), and cobalt (Harper et al., 2012). However, although elements such as selenium are important for many technological sectors, MFA analyses for these less-widely used elements have not been addressed, in part because of data limitations. This work is the first attempt to address the data challenges and quantify the cycle of selenium. It explores the historical

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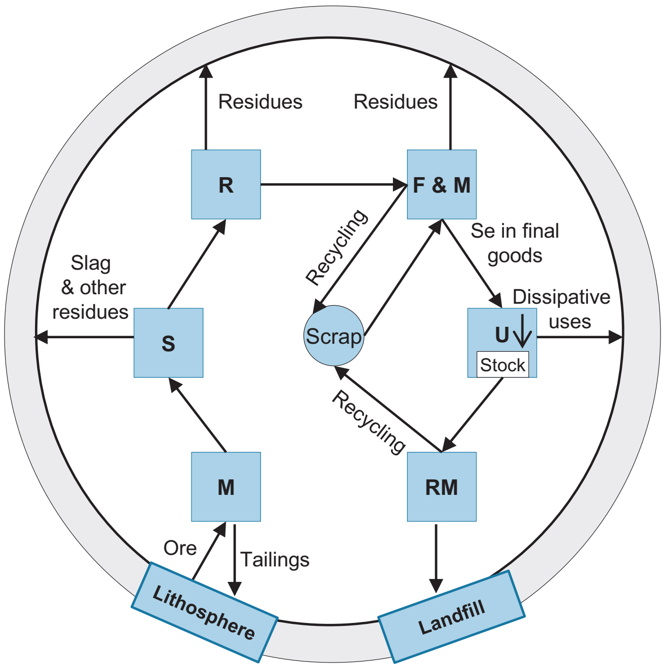

Fig. 1. Selenium cycle diagram. The main life stages include M = Mine, S = Smelter, R = Refinery, F&M = Fabrication and Manufacturing, U = Use, and RM = Resource Management.

global selenium cycles with the aim of informing resource planning for selenium, especially for emerging technologies.

2. Methodology

Selenium cycles are constructed by following the element through stages delineated as Production, Fabrication and Manufacturing, Use, and Resource Management. These stages are illustrated in the circular life cycle diagram in Fig. 1. Conservation of mass requires that the mass of total inputs to a stage equals the mass of total outputs plus the accumulation of materials at each time step, which is one year in our model.

The selenium cycles we have constructed are best regarded as informed estimates rather than exact values due to limitations and uncertainties in the existing data. One example of these limitations is that companies and countries withhold refinery data so as not to disclose proprietary information. In this work, we used the annual world refinery production figures published by U.S. Geological Survey (2011b), although the publication mentions that withheld data are not included in the totals. Also, the annual refinery production figures are assumed be equivalent to annual consumption. The production steps preceding refining are not particularly well documented either, because selenium recovery is usually a secondary objective to copper production.

Because copper production is the major source of selenium, and due to limited information for production from other metals, we track selenium flows only related to copper production, so our results are probably modest underestimates. The percentage of losses during production processes are assumed to be constant over the years in this work, due to lack of yearly data.

Besides the production processes, there are uncertainties regarding the other stages of the selenium cycle as well. Undocumented losses occur during fabrication and manufacturing; these were characterized based on informed estimates from industry sources. Additionally, the historical distribution of selenium into various end uses is also not readily available. We have estimated these factors for seven principal end uses based on various historical documents (see Supplementary Information for a detailed explanation of end-use percentages).

2.1. Production

Selenium is primarily a by-product of electrolytic copper refining (Hoffmann and King, 2010; U.S. Geological Survey, 2011a). Approximately 90% of selenium is obtained from anode slimes formed during the electrolytic refining of copper (Roskill Information Services, 1990). The rest is recovered from lead, zinc, nickel, silver, and lead ores (Hoffmann and King, 2010). Due to the dominance of the copper process in selenium recovery and the scarcity of data from other processes, the present work quantifies the selenium flows associated with copper production processes only. In our model, the Production stage includes the mining and beneficiation of the copper ore, smelting, and refining. The majority of the world copper refining uses electrolysis (Kundig and Dresher, 2010). This treatment yields copper at the cathode of the electrolytic cell, while the impurities accumulate at the bottom of the tank house as “anode slimes”. The anode slimes contain on average 2–25% selenium by mass, as well as tellurium and precious metals such as silver, gold, and platinum group metals at various percentages depending on the scarce metal content of the treated ore (Hoffmann and King, 2010). According to a 2006 survey of 56 worldwide electrolytic copper refiners, 52 plants reported selenium in their anode slimes (Moats et al., 2007), but only about 50% of this selenium is recovered on average (George, 2012).

The material flows during the production stage are calculated by tracking the refined selenium back to its source deposit and applying recovery and loss rates obtained from the literature (Ojebuoboh, 2008). As shown in the flow diagram in Fig. 2, the recovery rate during concentration is 10%, during smelting and converting is 50%, and during anode slimes treatment is 90%. If the refinery recovers the selenium in its anode slimes, the recovery efficiency of the anode slimes treatment is as high as 90% because the recovery process is usually optimized to recover as much material as possible, especially the precious metals, in the anode slimes (Ojebuoboh, 2012). Because of lack of data on changes in recovery efficiency over time, the efficiencies are assumed to be constant over time in the model. The selenium resulting from the anode slimes treatment process is called crude selenium, and enters the Fabrication and Manufacturing stage to be further processed for use in products.

2.2. Fabrication and manufacturing (F&M)

The selenium inflow to the Fabrication and Manufacturing (F&M) stage is separated into seven end-use sectors: glass manufacturing, chemicals and pigments, photoreceptors, rectifiers, photovoltaics, biological uses, and metallurgical uses. The inflow to F&M for the time period 1940–2010 is obtained from the historical world refinery production statistics published by the U.S. Geological Survey (2011b). It is assumed that the yearly refinery production is equivalent to the inflow to F&M in the same year. In order to quantify the selenium flowing into each end-use sector, the percentage distribution across end-use sectors is obtained from various historical industry reports as well as historical U.S. Geological Survey publications (see Table A.1 through Table A.4 in Supplementary Information for details).

At the Fabrication stage, crude selenium obtained from copper by-product plants is fabricated into commercial grade selenium (99.5% purity), with a loss rate of 5–10% based on industry estimates. For end-uses other than electronics, commercial grade selenium is transformed into the selenites of sodium, barium, or zinc to be used in glass, selenous acid to be used in electrowinning of manganese, sodium selenite to be used in animal feed, and selenium sulfide to be used in anti-dandruff shampoos (Hoffmann and