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Silver supply risk analysis for the solar sector

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A B S T R A C T

The anthropogenic silver cycle shows the global material flows of silver on an annual basis. Beginning with mine supply the silver flows in various end use sectors. It is either stored as part of the above ground silver reserves or gets consumed and recycled or dissipates on landfills or with sewage. The article discusses supply–demand scenarios of silver. The study is methodically based on an analysis of resource specific factors like exploration rates, reserves and resources and regional distribution of exploration areas.

Among the numerous application areas for silver the one with the greatest growth potential is discussed in detail. Solar energy sector is a fast growing area which is analysed quantitatively in detail to obtain information on potential future bottlenecks in material availability. Due to its' high electrical conductivity silver is used in silicon photovoltaic technology and Grätzel cells to form the electrical contacts. In concentrated solar power applications silver is the material of choice as the coating of the mirror because of its' high optical reflectivity. Both concerns about climate change as well as questions related to energy resources and energy security stress the importance of renewable energy technologies. This has resulted in several future scenarios with partly very ambitious goals for the construction of the new energy infrastructure. The scenarios are discussed in the light of known silver resources.

Keywords:

Silver reserves

Criticality assessment

Solar sector

Photovoltaics

Concentrated solar power

1. Introduction

Silver has many exceptional physical and chemical characteristics, which has resulted in an extensive use of silver through the mankind for several millennium. Silver has been used since at least 4000 BC for jewellery, silverware, vessels and sacral objects. First archeological finds in Egypt are dated back to 3500 BC, but silver has also been used among the Goths, Assyrians, Greeks, Romans, and Germans. In the Bronze Age, about 4000 years ago, silver gained its most important function of a monetary nature: first as hack-silver, later as ingots. Several characteristics of silver contributed to this evolution: silver represents a high monetary value on low volume, silver is virtually divisible in an unlimited fashion without losing on value, and it is stable in pure air and water. Lydians were the first to coin silver in the form of electrum (silver forming an alloy with gold) around 700 BC. Later pure silver

coins were developed. Well known early silver coins were the tetradrachm of the Athenian empire or the Roman denarius [1].

Silver has long been known to have antibacterial effects. Hippocrates, “the father of medicine” was aware of silvers healing functions [2]. Milk or water keeps longer fresh if a silver coin is added to the vessel [1]. During World War I silver was used for the wound treatment [3]. The use of nanosilver has created new applications in the hygiene and medical sector [4,5].

Silver halides are photosensitive and thus silver has formed the basis of photography before the digital age. A wide scale of applications in the electronics industry is based on high electrical conductivity of silver – highest of all metals. Both touch switches as well as conventional switches used in a wide range of electronic applications rely on silver. Silver based films and inks are used in printed circuits and RFID tags found in many consumer items. CDs, DVDs and plasma display panels are further examples in the electronics industry, where silver is consumed. Further technical applications are based on the highest thermal conductivity of silver amongst all metals (brazes and solders) and one of the highest optical reflectivities [6].

One of the fastest growing demand areas for silver is related to green energy technologies, promoted throughout the

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Abbreviations

S_{MC}	cumulative upper limit for installation of a technology
R	estimated metal reserve (reserve base)
F	metal requirement per capacity
G_{MC}	material constrained annual growth of the existing stock
$r(t)$	annual availability of the metal
$l(t)$	annual losses in manufacturing and recycling
ppb	parts per billion, one part in 10^9
ETF	exchange traded funds
EPIA	European Photovoltaic Industry Association
DSSC	dye-sensitized solar cells
OPV	organic photovoltaics
CSP	concentrated solar power
LFR	linear Fresnel reflector
CLFR	concentrating linear Fresnel reflector

industrialized world in order to tackle both climate change as well as energy security issues. If the future scenarios for green energy technologies published by several entities such as IPCC, European Commission or national governments, are going to become reality, it will gradually shift the energy sector from fossil towards renewable energy sources. However the harvesting of renewable energy sources is not possible without related technologies and therefore the current dependence on fossil fuels will be replaced by a dependence on several minerals and materials needed in the green technologies. Silver is one of the key minerals used in green energy technologies [7]. Because of its high electrical conductivity it is used in several photovoltaic technologies. Further it is found in mirrors used in concentrated solar power, CSP, thus making use of the high reflectivity of silver. Also on the energy consuming side we find green technologies, where silver is needed. Examples of such are electric vehicles, where the increase in electronics compared to combustion engine technology leads to an increase in silver demand [8].

2. Limits to silver based technologies – theoretical approach

Björn Andersson [9] formed a theoretical approach for estimating the possible material constraints for certain technologies and materials. His approach is twofold. A cumulative upper limit for a given technology based on key metal availability can be estimated based on worldwide resources as follows:

$$S_{MC} = R/F, \quad (1)$$

where S_{MC} is the cumulative upper limit for installation of a technology, R is the estimated metal reserve (or reserve base) and F is metal requirement per capacity or service unit of the technology. This approach has some clear limitations mainly since the mineral reserves are dependent of market prices and available mining and refining technology. Changes in the markets or available technology shift those reserves which are in the current situation unprofitable to profitable ones and therefore affect the overall picture. The estimation of resources might vary depending on geological knowledge. Also due to political or other interest, not all countries publish their estimated resources. However, the method can give us some indications, whether a given metal might become a bottleneck in production.

Material constrained annual growth of the technology analysed is given by:

$$G_{MC} = [r(t) - l(t)]/F, \quad (2)$$

where G_{MC} is the material constrained annual growth of the existing stock, i.e. the annual market volume of the technology, $r(t)$ is the annual availability of a metal, $l(t)$ are annual losses in manufacturing and recycling, and F is net metal requirement per capacity or service unit. Therefore, this is the material based upper limit of the annual production of a technology. This method is not so much complicated by unknown variables, since the annual mining and recycling for many metals are in most cases well known. However, it is only limited to an analysis with a relatively short-time perspective. Andersson gives several examples of employing this method [10–12].

3. The anthropogenic silver cycle

Fig. 1 illustrates the global anthropogenic silver cycle. The amount of silver that has been mined over the whole history of mankind was estimated in 2009 to be 1,400,000 metric tons (44,600 million ounces) [13]. The analyst house CPM has provided estimates on the end-uses of this silver volume. Approximately half of it has been used in industrial processes and ended up on landfills. 653,000 tons (21,000 million ounces) are estimated to exist in the form of jewellery, tableware, decorations, 25,000 tons (806 million ounces) as silver bullion and 19,000 tons (625 million ounces) as coins [13]. In Fig. 1 we use the value 44,500 tons for the above ground stocks. This refers to the estimated stocks of silver bullion and coins, which is the share of the existing silver that can easily flow into the market.

In 2010, the industry used almost 28,000 tons of silver, which is 6000 tons more than was mined in the same year [16]. The deficit, which has oscillated around the level of 6000 tons annually throughout the last decade, has been filled by recycling and drawing silver from above ground stocks. It should be noted, that a share of the needed 28,000 tons of silver actually ended up growing the above ground stocks in form of new bullion and coins. Each year some silver dissipates either through sewage (mainly silver used in medical or hygiene sector) or ending in the landfills.

3.1. Supply structure of silver

The annual silver markets are in the range of 35,000 metric tons. The basic source of silver in the world metals market is the mining sector, which accounts for approximately 65% share of the annual silver supply. Since silver demand exceeds the annual mine supply, there is a need to create flows from the above ground silver inventories to the market. Recycling of old jewellery, photographic wastewater and other industrial processes are responsible for one-third of the annual silver markets. In 2010, almost 12,000 tons of recycled silver came to the world market. Of this material flow roughly 1% comes from government disposals [16]. These shares have remained fairly stable over the last decade. Fig. 2 gives an overview of the supply situation.

3.1.1. Geological occurrence and mining

Silver belongs to the group of precious metals. Precious metals are naturally occurring rare metals, which have high economic value. In addition to silver and gold – the two most widely known precious metals – there are six other elements (ruthenium, rhodium, palladium, osmium, iridium, platinum) belonging to this group. Silver with a mass abundance of 75 ppb (parts per billion, one part in 10^9) is the most common precious metal in the Earth's

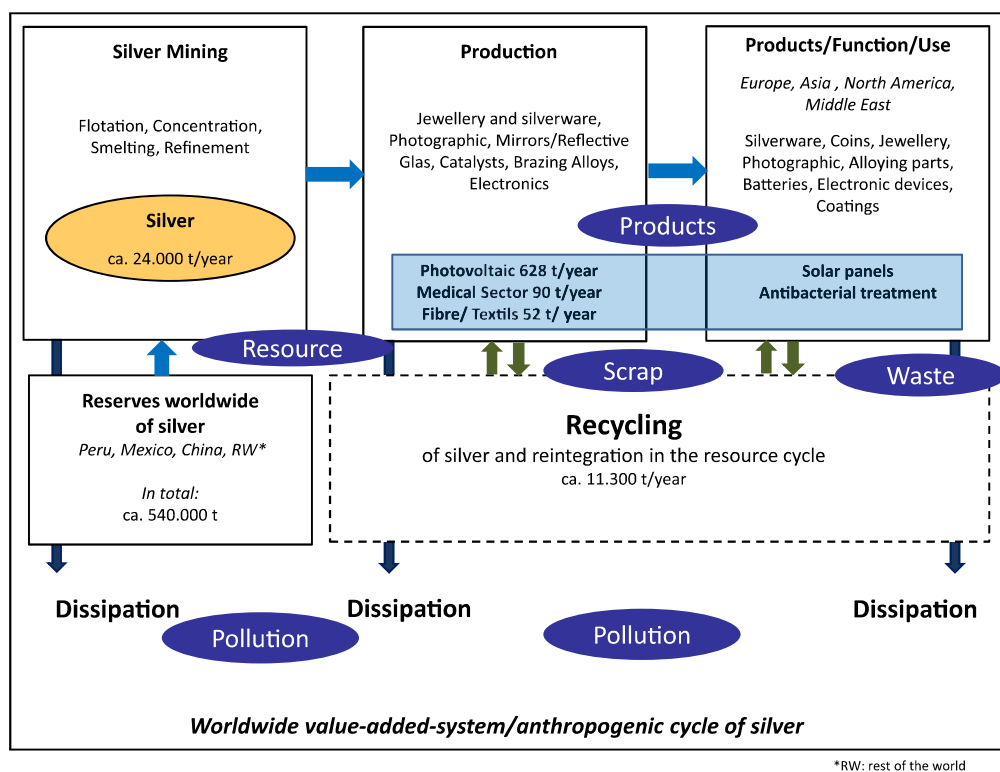


Fig. 1. Worldwide anthropogenic silver cycle. Volumes refer to 2011 and 2012 [14,15].

crust and about 20 times as common as gold with a mass abundance of 4 ppb [19].

Silver is found in several forms in nature. Only very rarely is it found in native form as nuggets. Other deposits which are principally worked for silver include argentite (Ag_2S) or tetrahedrite ($(\text{CuAg})_{12}\text{Sb}_4\text{S}_{13}$), but there are also other silver minerals such as chlorargyrite (AgCl) or pyrargyrite (Ag_3SbS_3) [20].

The chemical characteristics of silver are similar to copper, and thus silver can substitute copper on atomic level in most copper minerals. Silver also resembles lead. Therefore principal sources for silver as a by-product in mining industry are ores of copper, copper–nickel, lead and lead–zinc. Silver also forms an alloy with gold called electrum and is a desirable by-product in goldmines [20]. The world reserves of silver are estimated by USGS to be 540,000 metric tons assuming the current economics and mining and production practices [15].

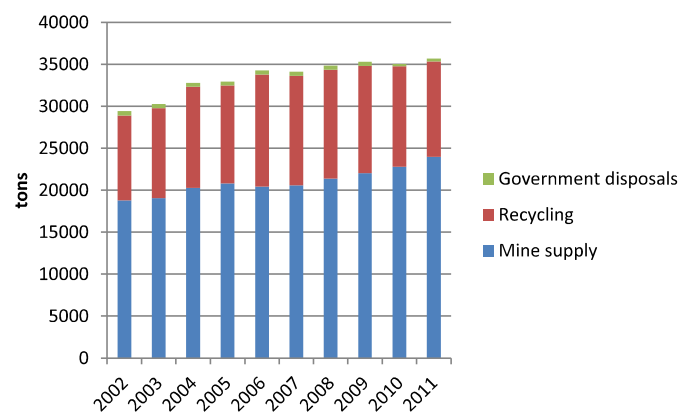


Fig. 2. Silver supply on the world metals market in 2002–2011 [17,18].

After mining, i.e. extraction of silver containing mineral from the lithosphere, silver is separated from other materials and refined to concentrate through various smelting and leaching processes. Some of the important processes include e.g. electrolytic copper refining and application of the Parkes process on lead metal [21].

Before World War II the silver supply from mining was fluctuating between 5000 and 8000 tons annually as indicated in Fig. 3. Since then its volume has risen by a threefold and amounts presently around 23,000 tons. Silver minerals are found in hydrothermal veins in volcanic rocks of andesitic and rhyolitic affinity. The great mountain chain on the West coast of North- and Latin-America is made up of andesitic and rhyolitic volcanoes and therefore around 75% of all silver mined comes from the Americas [20]. At present almost 30% of mine production is from North-

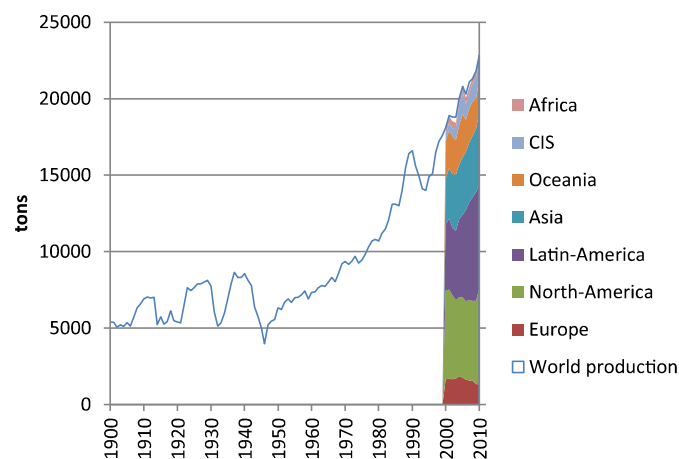


Fig. 3. Worldwide silver production between 1900 and 2010 [22–25].

America and another 30% from Latin-America (Peru, Chile). Asia accounts for 20% of the mine output with China taking care of half of the Asian production. The European silver mines (6% share of the world markets) are to a large degree located in Poland.

Primary silver production requires either native silver or a silver mineral and accounts for only one third of the world silver production as shown by Fig. 4. Silver forms a valuable by-product in lead/zinc mining industry (34% of silver production in 2010), for copper mines (23%) and in gold mining (12%).

3.2. Demand structure for silver

Fig. 5 shows an overview of the silver markets over the last decade.

One of the main applications for silver since 1850s has been photography. A silver halide is a compound formed between silver and one of the halogens, silver bromide, silver chloride, silver iodide or silver fluoride. Silver halides are highly photosensitive. The film or photographic paper is coated with a gelatin containing silver halides. When exposed to light, the silver halide turns black [27]. Photography was one of the main industrial applications of silver until recent years, when with the rise of digital technology the silver consumption has declined significantly, and in 2011 corresponded to only 11% of the total demand.

Due to its excellent electrical conductivity silver is used almost everywhere in electronics [14]. 23% of the silver demand in 2011 was due to this sector. Silver oxide batteries and silver–zinc batteries can be found, for example, in cameras, toys, hearing aids, watches, calculators, mobile phones and laptop computers. Printed circuit boards used in many consumer items like mobile phones or computers are produced with silver based inks or films. RFID tags (radio frequency identification) are produced with silver based inks and are found today in a broad variety of products. Silver membrane switches (touch switches) are found today in many consumer products and even conventional switches used for example in room lighting contain small amounts of silver. Other common every day products with a small silver content are CDs, DVDs and plasma screens [6].

Silver can form alloys with several other metals such as copper, zinc, tin, nickel or indium. Silver alloys are in general more rigid than pure silver. Alloys are used in a broad variety of applications such as high quality musical instruments, silver decorations, as conducting materials in condensators or contact material in relays. Silver brazing and soldering (5% of silver demand in 2011) is used in numerous ways in automobile and aerospace industries or electric

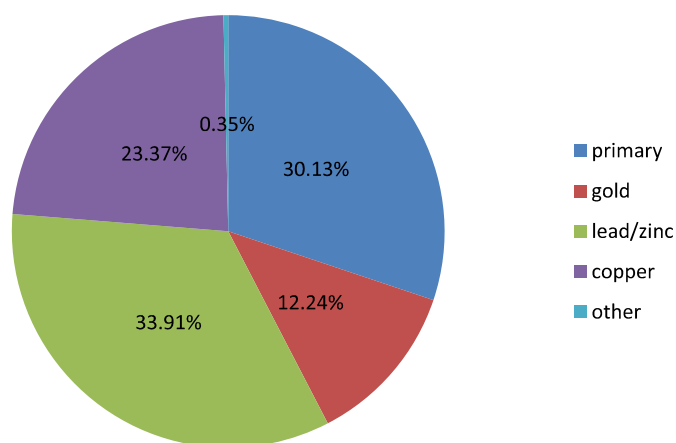


Fig. 4. Primary and secondary mine production of silver [26].

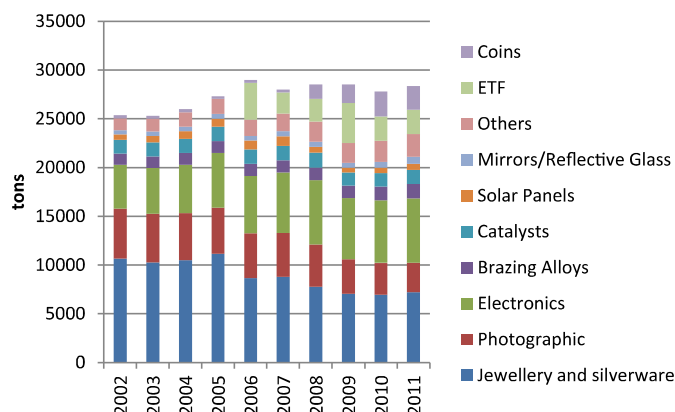


Fig. 5. Worldwide silver demand in 2002–2011 [17,18].

power distribution. Silver–tin solders are used in copper pipes in household replacing hazardous lead based solders [6].

Silver is needed for the production of ethylene oxide and formaldehyde, both being important raw materials in the plastics industry [6]. Silver acts as a catalyst in the production process, which means that it is not consumed by the process and can therefore be recovered and recycled to a large degree [28,29]. In 2011 5% of silver demand was due to catalysts [18].

When steel ball bearings are electroplated with silver, they become stronger and able to function at very high temperatures. Such bearings are used in many types of engines, where a continuous function at high temperatures is important, such as jet engines [6].

According to the VM Group [18] some application areas possess significant potential for growing silver demand in the future. If measured in quantitative terms the most important new and rapidly growing area of silver consumption is found in various green energy applications. Silver is used in photovoltaics technology, mainly in crystalline silicon solar cells, to form electrical contacts between the cells. Due to its superior optical reflectivity it is the first choice of material for high quality mirrors used in concentrated solar power systems. A similar application is a silver coated window which reflects the excessive solar radiation outward and thus reduces the need for air conditioning. Also electric cars demand more silver than conventional cars with combustion engine due to the increased amount of electronics [8].

Another group of expected increasing silver demand in future makes use of the long known effects of silver: it hinders the bacteria and fungi from growing [30]. Silver ions are known to damage the cell membrane of the bacteria thus causing the bacteria eventually to die [31]. Several applications make use of this characteristic of silver. Silver is used in water purifiers to provide potable water, the need of which is expected to grow in the future [18]. Several hygiene applications exist, like in the food processing and packaging chain or in washing machines, refrigerators or air conditioners [6]. In the medical sector the uses of silver are manifold. In the developing world X-ray technology is still based on silver halides. In industrialized nations the old X-ray technology has mostly been replaced by digital technology, but several other silver applications are expected to grow in demand as the population is ageing: wound care dressings, pacemakers, bone cement, sutures, grafts. Medical devices like needles, catheters, stethoscopes or surgical tools are coated with silver to prevent infections [32]. In the textile industry silver is used for impregnation. The effect of silver is to diminish body odour [18].

In addition, the financial crisis beginning in 2008 has woken the interest in silver as an investment. Thus in 2011 almost 20% of the

silver consumed was melted into coins or barrels bought directly by investors or backed up ETFs (exchange-traded funds).

3.2.1. Silver demand in the solar energy sector

3.2.1.1. Crystalline silicon photovoltaics. Crystalline silicon solar cells (c-Si) represent the first generation of photovoltaic technology. There are basically three types of c-Si cells: mono crystalline (mc-Si), polycrystalline (pc-Si), and ribbon silicon (ribbon pc-Si). The achieved efficiency of the cell depends on the technology, but is roughly 20% [33]. c-Si is still with a share of 80% the most common photovoltaic technology on the market, however its market share is gradually decreasing [34].

Silver is needed for the metallization of the modules. There is a wide variety of technical approaches. Feltrin describes [35] one widely used method of forming a top electrode with 20–80 micron thick silver fingers and covering 5% of the cell area. This leads to a silver consumption of 10–42 g/m². Electrons generated in the cell are collected by the fingers and conducted further to wider metal strips called busbars. Busbars connect the fingers in the cell and provide the electrical contact between the cells [34]. In this analysis we use silver consumption estimates published by the SEMI PV Group Europe and shown in Fig. 6.

Current silver consumption is estimated by the manufacturers to be approximately 10 g/m². Silver is one of the main cost drivers in the cell manufacturing process. The silver consumption will be reduced in the first place through reduction of the paste consumption. Beginning in 2015 the photovoltaic industry expects a gradual replacement of silver by a substitute, which is intended to be copper [36].

3.2.1.2. Dye sensitized solar cells, DSSC. Dye sensitized solar cells are a form of organic solar cells belonging to the third generation of photovoltaics, which have not yet been commercialized on a large scale. This technology has a number of advantages. First, the manufacturing of the cell is based on an inexpensive and simple low-cost method of conventional roll-printing. Second, the cells are semi-flexible and semi-transparent, which makes several new uses possible. The reported efficiency of the technology varies. European Photovoltaic Industry Association EPIA estimated the efficiency of the cells and modules in the range of 2%–4% [34], whereas Fraunhofer ISI reports 8% [37]. Green publishes a “noble exception” cell efficiency to be 11.4% [33].

Grätzel describes the working principle of the dye sensitized cell [38]. The photoactive medium is the dye, which absorbs the incoming light. It is anchored to the surface of a wide-band semiconductor. The electrons injected by photons in the dye are transported in the conduction band of the semiconductor, usually

titanium oxide (TiO₂). The electrochemical system lies between two glass plates. The inner surfaces of the glass plates are covered with a thin transparent conducting oxide (SnO₂). The cathode is generally platinum [37]. Single elements in the size of 0.6 m² are connected to each other with silver. Platinum acts as a catalyst.

The photosensitive dye can be based on several materials. However, the best performances are achieved by dyes based on a complex between ruthenium and osmium [39]. Fraunhofer ISI reports material consumption of ruthenium, platinum, and silver based on expert estimations [37] as shown in Table 1. Silver is used for the metallization of the cells.

3.2.1.3. Organic photovoltaics, OPV. Organic photovoltaics are another interesting solar technology which is based on organic electronics. The technology shows some very promising features, which make it an interesting solar technology for the future. The manufacturing method, which is based on roll-to-roll processing, is very fast allowing a high production capacity. The energy pay-back time has shown to be as short as 180 days in southern Europe [40]. The technology needs silver for the collection and conduction of electricity, however the recycling rate is shown to be as high as 95% [41]. This type of solar cell can be installed not only on land but also in marine and airborne conditions [42].

3.2.1.4. Concentrated solar power – CSP. Concentrated solar power systems comprise systems of mirrors or lenses that concentrate solar light into a small area. The concentrated light is converted into heat, which produces electricity with conventional technology. Silver is essential for this technology, since due to its superior light reflectivity characteristics it is the first choice of material for such mirrors.

3.2.1.4.1. Parabolic trough. A parabolic trough is the most commonly used CSP technology. It consists of a linear parabolic reflector and a receiver tube, which follows the reflector's focal line. Sunlight is concentrated on the focal line of the linear parabolic reflector. The working fluid (molten salt or synthetic oil) is heated to 150–350 °C, when it moves along the tube. The fluid is then used to heat steam in a standard generator. A parabolic trough is usually oriented on the north–south axis and it tracks the sun's movement over the day. The efficiency for the whole conversion cycle, i.e. the electrical output versus impinging solar energy on the reflector is roughly 15% [43].

3.2.1.4.2. Linear Fresnel reflectors. Linear Fresnel reflectors (LFR) are made of long thin mirror segments which reflect the sun light onto an absorber tube. The tube is fixed in space above the mirror field and located in the focal point of the reflector. The reflector is based on the Fresnel lens effect, originally used in light houses. This effect allows a large aperture and a short focal length, which in turn means less material requirements and thus lower costs for the reflector. Fresnel reflectors are used in CSP systems of various sizes. A concentrating linear Fresnel reflector (CLFR) is a special type of reflector, which uses multiple absorbers instead of one. Mills reports an energy conversion efficiency of 19% from incoming solar radiation to electricity [44].

3.2.1.4.3. Solar power tower. A solar power tower, also called heliostat power plant, consists of a system of flat mirrors

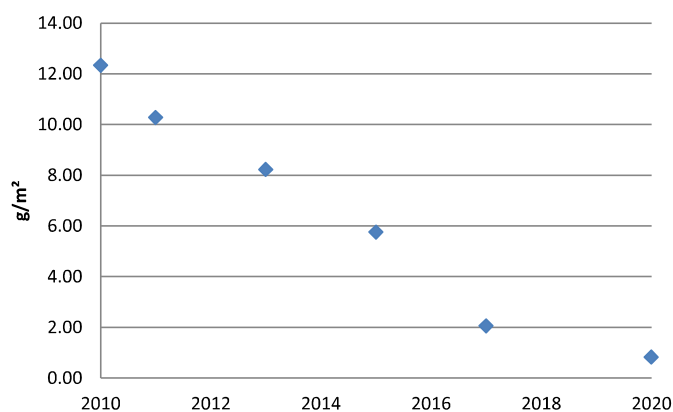


Fig. 6. Silver consumption per area in c-Si cells [36].

Table 1
Material consumption of some selected raw materials in dye-sensitized solar cells [37].

Material	Needed mass/area [g/m ²]
Ruthenium	0.07
Platinum	0.03
Silver	1

(heliostats) tracking the sun along two axes. The absorber fluid, originally water but more recently molten salts, is located in a tower, which receives the focused sunlight. The absorber fluid is heated to 500–1000 °C. It can either be directly used to generate steam and power a turbine or it can be stored for later electricity generation. Therefore a solar power tower can produce electricity also when the sun is not shining. Mills has reported energy conversion efficiencies from 5.6% to 17% from incoming solar insolation to electricity [44].

3.2.1.4.4. Dish stirling. Dish stirling systems are typically run as stand-alone systems with a maximum electricity generation capacity of 50 kW. It consists of a parabolic reflector that tracks the sun along two axes. The working fluid is positioned in the focal point, which is heated to 250–700 °C. The fluid runs a Stirling engine, which is as well situated in the focal point. The dish stirling systems reach the highest solar energy to electricity conversion efficiencies, varying between 20% and 30% [44]. On the other hand, the heavy stirling engine is part of the movable system, and therefore a rigid and a strong frame and tracking system is needed.

3.2.1.4.5. Silver in CSP systems. Silver is used to obtain the high reflectance of the mirrors. The required silver per mirror area is constant for all technologies (1 g/m²) but since the system efficiency is dependent on the technology, the silver requirement with respect to electricity generation capacity varies. Table 2 gives silver requirements for concentrated solar power technologies.

3.3. Recycling of silver and reintegration in the resource cycle

During the last decade silver demand has been 20%–30% higher than the annual mine supply. The resulting market deficit has been satisfied by recycling silver scrap. Fig. 7 summarizes the global flows of silver scrap. Photography has been originally the main source for recycled silver. According to the USGS the recycling rate varies between 20% and 100% depending on photographic material [45]. However due to the rise of digital technology this sector provided less than 20% of the recycling volumes in 2011. Jewellery and old coins form another source of recycled silver. Industrial sources of silver consist mainly of electronics scrap: computers, telecommunications and consumer electronics. It has been estimated that the silver content in electronic scrap varies from 0.02% to 0.5% [45]. In chemical industry the main use of silver is in catalytic form. USGS estimates the recycling rate to be more than 98% [45]. The end-of-life catalyst is sent to the catalyst manufacturer, who takes the responsibility for the recycling.

Lifespan expectations for PV panels vary between 20 and 40 years but are given usually to be 30 years [46]. Several recycling processes are being developed for PV panels whereas only two processes are in operation. Deutsche solar's process is used for crystalline silicon panels whereas First solar's process is mainly used for CdTe panels [47]. PV Cycle is an association, which has been created by the European solar industry in 2007. It runs a PV recycling programme through 91 collection points in Europe [47].

Lee describes various recycling processes for silver in PV panels [48]. Silver can be recovered either through electrolysis or through precipitation when dissolved in a leaching solution. Silver can also be recovered using metallic replacement method. The recovery rate

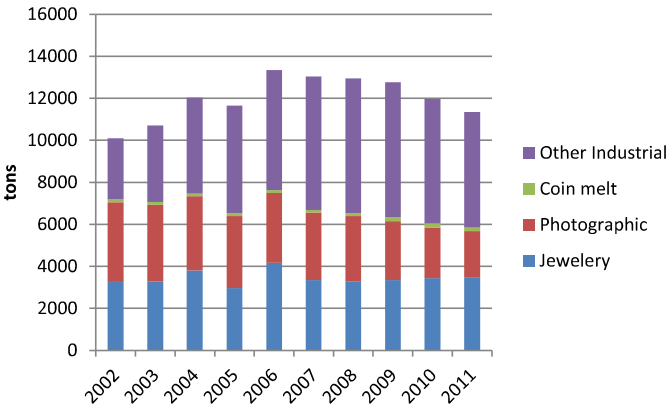


Fig. 7. Sources of recycled silver [17,18].

for silver is estimated to be 98%–100%. The scrap from silicon solar panels was estimated to have a 1.67 w% silver content [48]. Another estimation for the silver content in scrap is 1% [47]. A research by Technical University of Denmark reports a 95% yield of silver for OPV. The shredded solar cells are treated with nitric acid and the silver is recovered in form of silver chloride [41].

Some of the silver that has been used in the production cycle ends with waste on landfills or sewage and dissipates in nature. This is usually the case for silver used in medical applications, hygiene articles or in the textile industry, where the amount of silver per item is very small and thus recycling is impossible.

4. Results

4.1. Material constrained stock in the solar sector

According to USGS the worldwide silver reserves, i.e. the part of silver resources that can be economically extracted at current time, are estimated to be 540,000 tons. USGS does not give any estimation for global resources [15].

In 2011, 2.2% of world silver demand was consumed in the manufacturing of solar panels and 2.5% in the manufacturing of mirrors and reflective glass. We assume two alternative cases. The first one reflects the current market situation by assuming that 2% of the silver available will be consumed in the PV sector and 2% in the CSP sector. In the other scenario we assume a substantially higher market share of 5% for both PV and CSP.

Applying Equation (1) we can compute an upper limit for the cumulative installation of each given technology. The matrix gives the estimated electricity generation potential for the given technology in four different cases: 2% market share and 5% market share of the current reserves of 540,000 tons.

For crystalline silicon solar cells we assume a silver requirement of 8.2 g/m² (estimated requirement for 2020 is 0.82 g/m² after substitution with copper), an electricity generation efficiency of 20%, and a solar insolation of 2000 kWh/m²/annum. The results are shown in Table 3.

Table 3
The upper limit for the annual electricity production based on crystalline silicon photovoltaic cells. For comparison the world electricity demand in 2010 was 21,431 TWh [49].

	2% Market share	5% Market share
Reserves 540,000 tons	10,800 tons	27,000 tons
Silver requirement 8.2 g/m ²	530 TWh	1310 TWh
Silver requirement 0.82 g/m ²	5300 TWh	13,100 TWh

Table 2
Silver requirement for the various concentrated solar power technologies [37].

	Silver content [kg/m ²]	kg/MW
Fresnel reflector	0.001	13.75
Parabolic trough	0.001	3.75
Solar power tower	0.001	7.57

Table 4

The upper limit for the annual electricity production based dye sensitized solar cells. For comparison the world electricity demand in 2010 was 21,431 TWh [49].

	2% Market share	5% Market share
Reserves 540,000 tons	10,800 tons	27,000 tons
DSSC annual el. production	1730 TWh	4320 TWh

Table 5

The upper limit for the annual electricity production based on Fresnel reflectors and parabolic troughs. For comparison the world electricity demand in 2010 was 21,431 TWh [49].

	2% Market share	5% Market share
Reserves 540,000 tons	10,800 tons	27,000 tons
Fresnel reflector	1100 TWh	2800 TWh
Parabolic trough	6000 TWh	14,900 TWh

Dye sensitized solar cells show currently an electricity generation efficiency of 8%. The technology needs in addition to silver also ruthenium, which belongs to the group of rare earth elements. The annual production of ruthenium is 20 tons and the reserves are estimated to be 5000 tons [50]. Material consumption of silver and ruthenium are 1 g/m² and 0.07 g/m² respectively [37]. Assuming a solar insolation of 2000 kWh/m²/annum and employing Equation (1) the upper limits for electricity generation with DSSC are given in Table 4.

We have chosen two technologies to represent the concentrated solar power sector: Fresnel reflectors and parabolic troughs, since these technologies are currently the most common in the market.

The needed amount of silver per installed capacity is different for the Fresnel reflector (13.75 kg silver/MW) and parabolic trough (3.75 kg silver/MW) [37]. The conversion of nominal power to annual electricity production varies depending on the technical construction of the power plant. Thus we have chosen the SEGS plant at Kramer Junction in California to represent the parabolic trough technology. Long term operational data shows an annual electricity production of 2.1 MWh/MW nominal power [51]. Fresnel reflectors represent a newer technology, here we choose the first commercial power plant in Europe, Puerto Errado 1 in Spain, to represent this technology. This power plant generates 1.4 MWh of electricity per 1 MW nominal power [52]. The results are presented in Table 5.

4.2. Material constrained growth in the solar sector

Equation (2) allows us to estimate the material constraints for the annual growth of the existing technology base. Annual silver mining is estimated to be 24,000 tons/annum [15]. We calculate

Table 6

Material constrained annual growth for c-Si PV cells, concentrated solar power applications and dye sensitized solar cells. DSSC is limited by the availability of ruthenium.

	2% Market share	5% Market share
Annual mining 24,000 tons	480 tons	1200 tons
c-Si PV		
Silver requirement 8.2 g/m ²	20 TWh	60 TWh
Silver requirement 0.82 g/m ²	230 TWh	580 TWh
CSP		
Fresnel reflector	50 TWh	130 TWh
Parabolic trough	270 TWh	660 TWh
DSSC		
Ruthenium limiting factor 29 km ² /year	5 TWh	
maximum installed capacity annually		

again two alternative cases, one with a 2% share of the silver market and one with a 5% share. Results are summarized in Table 6.

DSSC needs 0.07 g of ruthenium and 1 g silver per 1 m² of collector area as given in Table 1. The annual mining of ruthenium is 20 tons. Since DSSC is not yet produced on a commercial scale we cannot estimate what share of the available ruthenium might flow into this sector. Other competing uses of ruthenium are in the chemical industry, electronics and electrochemical processes. However if we make a very optimistic assumption that 10% of the annually available ruthenium could be used for DSSC, we obtain that annual DSSC production is limited by ruthenium to 29 km² which equals 5 TWh annual electricity production.

5. Discussion and conclusions

Results from previous sections are summarized in Fig. 8. We can assume that the solar energy sector will keep its market share in the future in the range of 2% of the available silver. Silver demand in photography is constantly decreasing, but at the same time other competing markets like the medical sector or the electrical industry are expected to remain strong and even grow. Fig. 8 compiles together the results of the previous chapter showing the level of electricity generation possible with silver dependent solar technologies. For comparison the global electricity generation in 2010 is given.

If we take the current known reserves of 540,000 tons of silver as basis for our calculations we can produce from 260 to 6000 TWh electricity annually with silver dependent technologies, depending on the technology chosen. The parabolic trough technology seems to possess the highest electricity production potential with respect to silver, i.e. some 6000 TWh annually. This is approximately 28% of the current global electricity production. Increasing the market share of the solar sector from current 2% to 5% – which seems unrealistic – the electricity potential increases 2.5 times, varying between 1300 and 15,000 TWh/a.

Several future scenarios have been published for the evolution of green energy technologies. Some of them have been analysed by IPCC as possible mitigation strategies in the climate change process [53]. Table 7 and Fig. 9 show these scenarios.

The IPCC report uses four different scenarios starting with IEA WEO 2009 as a basis scenario and ending in the Energy [r]evolution 2010 scenario and ReMIND-RECIPE with the most ambitious goals. PV and CSP are treated separately. However, there is no separation between the various technologies in these groups. Both the IEA

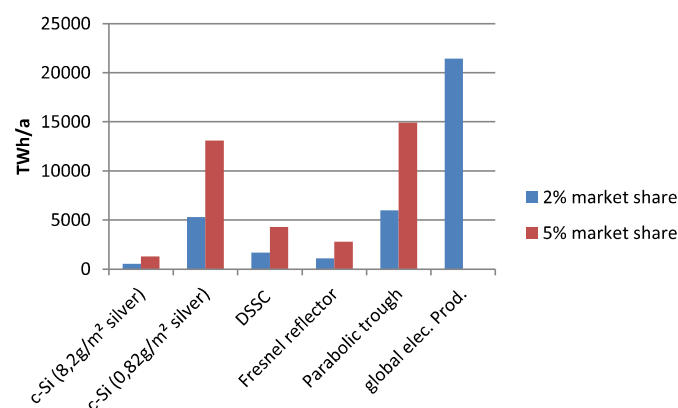


Fig. 8. Possible annual electricity production by the different solar technologies when assuming reserves of 540,000 tons of silver. Blue colour marks a 2% market share in silver and red 5% market share. The chart shows for comparison the global electricity production in 2010. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 7

Four scenarios by IPCC for the construction of solar energy infrastructure.

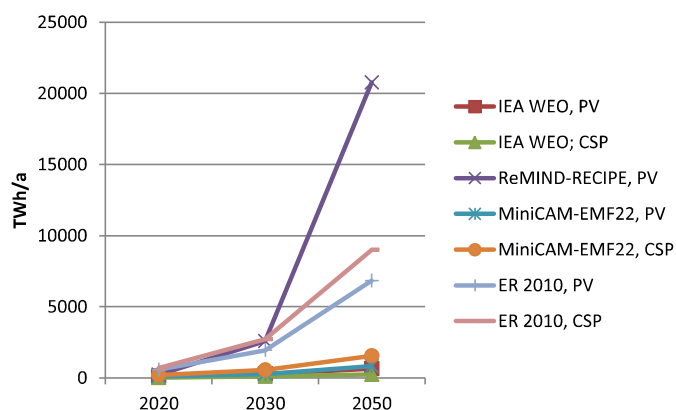
TWh/a	IEA WEO 2009	ReMIND- RECIPE	MiniCAM- EMF22	ER2010 – advanced
PV 2020	111	222	111	583
PV 2030	278	2583	278	2944
PV 2050	639	20,778	833	6833
CSP 2020	28	N/A	194	694
CSP 2030	111	N/A	556	2722
CSP 2050	250	N/A	1556	9000

WEO 2009 as well as MiniCAM-EMF22 scenarios are realistic in relation to available silver resources. However the maximal cumulative CSP generation capacity outlined by the ER scenario for 2030 is only possible to achieve with the parabolic through technology and the goal for 2050 requires 50% higher silver reserves as are known today. Only if we assume a 5% market share in silver for CSP technologies can this goal be achieved. Another possibility might be the substitution of silver by aluminium as a reflective material. This however would lead to a reduction in reflectivity of the mirror area, and thus the overall efficiency of the system would be reduced. For compensation a larger area is needed, which results in higher construction expenses.

The situation is similar for PV technologies. The cumulative capacity found in ReMIND-RECIPE for the year 2050 would need 4-fold silver reserves in order to be realistic when based on silver containing technologies. This requires the implementation of the least silver intensive PV technology, c-Si cell with 0.82 g/m² silver content. This low silver demand however will not be available at the market until 2020 according to SEMI PV Group. In ER 2010 the target for 2030 seems realistic, but only when assuming the low silver content of 0.82 g/m² in c-Si technology with substitution by copper. The cumulative PV capacity aimed for 2050 by ER 2010 exceeds again known silver reserves. However, there are other PV technologies, such as CIS, CdTe or a-Si that do not contain any silver. Nevertheless, these technologies face other bottlenecks in materials availability such as tellurium, indium or germanium.

Another interesting aspect to discuss is the annual solar markets and the growth needed in order to achieve the targets given by the scenarios. Opening new mines is typically very time consuming and can occur only after successful exploration activity. Therefore we can assume that the annual mining capacity cannot be exceeded from the current level during a timeframe of 5 years.

We calculated the needed annual growth rates of the PV and CSP markets in order to reach the targets set for 2020 by the various scenarios. The growth rates are listed in Table 8.

**Fig. 9.** Four scenarios by IPCC for the construction of solar energy infrastructure.**Table 8**

Annual growth rates needed by the various scenarios.

	IEA – WEO	ReMIND-RECIPE	MiniCAM-EMF 22	ER 2010
PV	4%	13%	4%	25%
CSP	29%	N/A	56%	76%

The various CSP technologies rely on silver, currently there are no silver free alternatives. An annual growth rate of 29%–76% would thus mean that in the short run other silver demanding markets should diminish in order to let CSP grow in such an aggressive manner. To be able to analyse how realistic this is, a cost structure of CSP in comparison to the cost structure of the competing markets is needed, i.e. the share of silver in the end products cost structure for CSP and the competing sectors is asked. Such an analysis goes beyond the scope of this article, however one can note, that during the last decade spot price of silver increased from 5 US\$ to 22 US\$ currently due to increased demand. Therefore it seems realistic to note, that an aggressive expansion of the CSP markets in the short run seems only possible through substitution by aluminium.

The photovoltaic market has seen in the past decade very high annual growth rates varying between 8% and 80% with an average of 42% [54]. If such high growth rates should in the future be based on technologies containing silver, this requires a rapidly decreasing silver content in the panels, as outlined by SEMI PV Group.

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References

- [1] Ludwig G, Wermusch G. Silber, Der Weg des Silbers von den Anfängen der Zivilisation bis zur Gegenwart. Berlin: Verlag Die Wirtschaft; 1988.
- [2] Grammaticos PC, Diamantis A. Useful known and unknown views of the father of modern medicine, Hippocrates and his teacher Democritus. *Hell J Nucl Med* 2008;11(1):2–4.
- [3] Borsuk DE, Gallant M, Richard D, Williams HB. Silver-coated nylon dressings for pediatric burn victims. *Can J Plast Surg* 2007;15(1):29–31.
- [4] Nowack B, Krug HF, Height M. 120 Years of nanosilver history: implications for policy makers. *Environ Sci Technol* 2011;45:1177–83.
- [5] Chaloupka K, Malam Y, Seifalian AM. Nanosilver as a new generation of nanoparticle in biomedical applications. *Trends Biotechnol* 2010;28(11):580–8.
- [6] Silver Institute. <http://www.silverinstitute.org/site/silver-in-industry/> [accessed 24.01.13].
- [7] Moss RL, Tzimas E, Kara H, Willis P, Kooroshy J. Critical metals in strategic energy technologies. Assessing rare metals as supply-chain bottlenecks in low carbon energy technologies. JRC Scientific and Technical Reports 65592. Luxembourg: Publications Office of the European Union; 2011.
- [8] Buchert M, Schueler-Hainsch E, Goldmann D, Treffer F. Ressourceneffizienz und ressourcenpolitische Aspekte des Systems Elektromobilität. Arbeitspaket 7 des Forschungsvorhabens OPTUM: Optimierung der Umwelteinlastungspotenziale von Elektrofahrzeugen. <http://www.oeko.de/oekodoc/1334/2011-449-de.pdf>; 2011.
- [9] Andersson BA. Material constraints on technology evolution: the case of scarce metals and emerging energy technologies. Doctoral thesis. Chalmers University of Technology and Göteborg University; 2001., http://bscw-app1.ethz.ch/pub/bscw.cgi/d170262/Andersson_2001.pdf.
- [10] Andersson BA, Azar C, Holmberg J, Karlsson S. Material constraints for thin-film solar cells. *Energy* 1998;23:407–11.
- [11] Andersson BA. Materials availability for large-scale thin-film photovoltaics. *Prog Photovolt* 2000;8:61–76.
- [12] Andersson BA, Jacobsson S. Monitoring and assessing technology choice: the case of solar cells. *Energy Policy* 2000;28:1037–49.
- [13] Schulte T. Silber das bessere gold. Rottenburg: KOPP Verlag; 2010.
- [14] GFMS. The future of silver industrial demand <http://www.silverinstitute.org/images/stories/silver/PDF/futuresilverindustrialdemand.pdf>; 2011.

- [15] USGS. Silver statistics, mineral commodity summaries <http://minerals.usgs.gov/minerals/pubs/commodity/silver/mcs-2013-silve.pdf>; 2013 [accessed 13.04.13].
- [16] ABN Amro Bank N.V., VM Group. The silver book <http://www.virtualmetals.co.uk/pdf/ABNSB0711.pdf>; 2011.
- [17] Fortis Bank Nederland, VM Group. Silver book <http://www.virtualmetals.co.uk/pdf/FSB080100.pdf>; 2008.
- [18] Fortis Bank Nederland, VM Group. Silver book <http://www.virtualmetals.co.uk/pdf/FBNSB0610.pdf>; 2010.
- [19] Abalakin V. Astronomical constants, abundance of elements in the earth's crust and in the sea. In: Lide DR, editor. CRC handbook of chemistry and physics. Boca Raton, Florida: CRC Press; 2005. p. 14.
- [20] Craig JR, Vaughan DJ, Skinner BJ. Resources of the earth. Origin, use, and environmental impact. 3rd ed. New Jersey, USA: Prentice Hall; 2001.
- [21] Johnson J, Jirikowic J, Bertram M, vyn Beers D, Gordon RB, Henderson K, et al. Contemporary anthropogenic silver cycle: a multilevel analysis. *Environ Sci Technol* 2005;39:4655–65.
- [22] USGS. Silver statistics, world mine production 1900–2009. <http://minerals.usgs.gov/ds/2005/140/silver.pdf> [accessed 10.09.12].
- [23] USGS. 2011 minerals yearbook. Silver [Advance Release]. <http://minerals.usgs.gov/minerals/pubs/commodity/silver/myb1-2011-silve.pdf> [accessed 10.09.12].
- [24] USGS. 2007 minerals yearbook. Silver. <http://minerals.usgs.gov/minerals/pubs/commodity/silver/myb1-2007-silve.pdf> [accessed 10.09.12].
- [25] USGS. 2003 minerals yearbook. Silver. <http://minerals.usgs.gov/minerals/pubs/commodity/silver/silvemyb03.pdf> [accessed 10.09.12].
- [26] GFMS. World silver survey 2010, a summary. <http://www.silverinstitute.org/site/wp-content/uploads/2011/07/wss10sum.pdf> [accessed 10.12.12].
- [27] Belloni J. The role of silver clusters in photography. *C R Phys* 2002;3:381–90.
- [28] Qian M, Liauw MA, Emig G. Formaldehyde synthesis from methanol over silver catalysts. *Appl Catal A Gen* 2003;238:211–22.
- [29] Dhalewadikar SV, Martinez EN, Varma A. Complex dynamic behaviour during ethylene oxidation on a supported silver catalyst. *Chem Eng Sci* 1986;41(7):1743–6.
- [30] Lansdown ABG. Silver in healthcare: its antimicrobial efficacy and safety in use. Royal Society of Chemistry; 2010. ISBN 1-84973-006-7. p. 159.
- [31] Li WR, Xie XB, Shi QS, Zeng HY, Ou-Yang YS, Chen YB. Antibacterial activity and mechanism of silver nanoparticles on *Escherichia coli*. *Appl Microbiol Biotechnol* 2010;85(4):1115–22. <http://dx.doi.org/10.1007/s00253-009-2159-5>.
- [32] Maillard J-Y, Hartemann P. Silver as an antimicrobial: facts and gaps in knowledge. *Crit Rev Microbiol* 2013;39(4):373–83. <http://dx.doi.org/10.3109/1040841X.2012.713323>.
- [33] Green M, Emery K, Hishikawa Y, Warta W, Dunlop ED. Solar cell efficiency tables (version 39) *Prog Photovolt Res Appl* 2012;20:12–20.
- [34] EPIA, Solar generation 6. Solar photovoltaic electricity empowering the world 2011. <http://www.epia.org/index.php?id=18> [accessed 13.03.13].
- [35] Feltrin A, Freundlich A. Material considerations for terawatt level deployment of photovoltaics. *Renew Energy* 2008;33:180–5.
- [36] Semi PV Group Europe. International Technology Roadmap for Photovoltaics (ITRPV.net) results 2011. http://www.itrpv.net/doc/roadmap_itrpv_2012_full_web.pdf [accessed 03.03.13].
- [37] Angerer G, Erdmann L, Marschneider-Weidemann F, Scharp M, Lüllmann A, Handke V, et al. Rohstoffe für Zukunftstechnologien. Einfluss des branchenspezifischen Rohstoffbedarfs in rohstoffintensiven Zukunftstechnologien auf die zukünftige Rohstoffnachfrage. Stuttgart, Germany: Fraunhofer IRB Verlag; 2009.
- [38] Grätzel M. Dye-sensitized solar cells. *J Photochem Photobiol C Photochem Rev* 2003;4(2):145–53.
- [39] Gao F, Wang Y, Zhang J, Shi D, Wang M, Humphrey-Baker R, et al. A new heteroleptic ruthenium sensitizer enhances the absorptivity of mesoporous titania film for a high efficiency dye-sensitized solar cell. *Chem Commun* 2008;23:2635–7.
- [40] Krebs FC, Espinosa N, Hösel M, Søndergaard RR, Jørgensen M. Rise to power – OPV-based solar parks. *Adv Mater* 2014;26:29–39.
- [41] Søndergaard RR, Espinosa N, Jørgensen M, Krebs FC. Efficient decommissioning and recycling of polymer solar cells: justification for use of silver. *Energy Environ Sci*; 2014. <http://dx.doi.org/10.1039/C3EE43746A>.
- [42] Espinosa N, Hösel M, Jørgensen M, Krebs FC. Large scale deployment of polymer solar cells on land, on sea and in the air. *Energy Environ Sci*; 2014. <http://dx.doi.org/10.1039/C3EE43212B>.
- [43] Duffie JA, Beckman WA. Solar engineering of thermal processes. New York, USA: John Wiley & Sons, Inc.; 1991.
- [44] Mills D. Advances in solar thermal electricity technology. *Sol Energy* 2004;76(1):19–31.
- [45] Hilliard HE. Silver recycling in the United States in 2000. US Geological Survey Circular 1196-N, <http://pubs.usgs.gov/circ/c1196n/c1196n.pdf>; 2003.
- [46] Branker K, Pathak MJM, Pearce JM. A review of solar photovoltaic leveled cost of electricity. *Renew Sustain Energy Rev* 2011;15:4470–82.
- [47] Monier V, Hestin M. Study on photovoltaic panels supplementing the impact assessment for a recast of the WEEE directive. Bio Intelligence Service, European Commission DG ENV; 2011. Contract ENV.G.4/FRA/2007/0067, <http://ec.europa.eu/environment/waste/weee/pdf/Study%20on%20PVs%20Bio%20final.pdf>.
- [48] Lee C-H, Hung C-E, Tsai S-L, Popuri SR, Liao C-H. Resource recovery of scrap silicon solar battery cell. *Waste Manage Res*. Published online 4 March 2013. <http://www.ncbi.nlm.nih.gov/pubmed/23460539>.
- [49] IEA. Key world energy statistics <http://www.iea.org/publications/freepublications/publication/kwes.pdf>; 2012.
- [50] Emsley J. Nature's building blocks: an A-Z guide to the elements. Oxford, UK: Oxford University Press; 2003. pp. 368–70.
- [51] Kolb JG. Evaluation of power production from the solar electric generating systems at Kramer junction: 1988 to 1993. Albuquerque, NM (United States): Sandia National Laboratories; 1994. Report Nr. SAND-94-2909C; CONF-950336-11, http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=10106411.
- [52] Novatec Solar. <http://www.novatecsolar.com/49-0-PE-1.html> [accessed 12.12.12].
- [53] Metz B, Davidson OR, Bosch PR, Dave R, Meyer LA, editors. Climate change 2007: mitigation of climate change. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press; 2007.
- [54] EPIA. Global market outlook for photovoltaics 2013–2017. http://www.epia.org/index.php?eID=tx_nawsecured1&u=0&file=/uploads/tx_epiapublications/GMO_2013_-_Final_PDF.pdf&t=1369939508&hash=6dd0244245ed3c05b93b89ed03ca4e6206cd57e9 [accessed 13.03.13].