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REVIEW ARTICLE

# Purification principles and methodologies to produce high-purity tellurium

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**ABSTRACT**
This review paper reconstructs the current development of tellurium purification technologies with their setups to obtain high-purity tellurium. Since the uptrend of the solar industry in the early 2000s, the demand for tellurium, especially high-purity quality, has increased sharply to enable the production of e.g. solar modules, solar panels and semiconductor. This paper focuses on both primary as well as secondary routes of purification. Especially the recycling aspects can contribute to a close-to-zero-waste process and circular economy horizons. For this purpose, a general introduction on tellurium sources and global primary production along with price trends were provided to show the path up to high purity grades. Recovery processes through secondary sources such as CdTe and $Bi_2Te_3$ were introduced, followed subsequently by a thorough review on two refining methods for tellurium. Vacuum distillation and zone refining processes were discussed in terms of their effectiveness in purifying tellurium as well as their challenges by reviewing relevant research. Through this review, several knowledge gaps can be identified to motivate further development of refining processes.

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## 1. Introduction

In the 90s, tellurium was mainly used as an additive for the enhancement of mechanical properties of steel. Since then, tellurium has been positively ranked in the solar energy industry, due to cutting-edge generation of CdTe photovoltaic cells, a valuable alternative among other prototypes from prices and yield point of view. Since 2002, the commercialisation of CdTe solar cells has led to a rapid increase in demand and is now the main application of this metalloid. During the development of semiconductor electronics, many studies have been developed about semiconductors. In terms of manufacturing, tellurium is mainly obtained as a byproduct from anode sludge, produced by electrolytic refining of copper. Metallurgical grade (i.e. 3N pure) metal is used in all common applications, except for semiconductor materials e.g. CdTe and $Cd_xHg_{1-x}Te$, $Zn_xCd_{1-x}Te$ that require higher purity levels. The use of high-purity starting materials is crucial for current advances of II–VI compound semiconductors technology and regarding solid solution, with good electrical properties. Thus, the required purity of input materials for fabricating high-performance devices is 6N or above and is growing to 7N due to the demand for better properties.

### 1.1. Main applications of tellurium

Tellurium is mainly used as a semiconductor in combination with cadmium to produce cadmium-telluride solar cells. Since this tellurium contains extremely low amounts of impurities, the degree of purity is described in functional terms as ‘nines’. Assuming a metal sample with a total impurity of 10 ppmw is to be classified under the functional terms of ‘nines’, it would then be 5N, which corresponds to 99.999%. The boundary between each ‘nines’ is determined by this single digit amount of impurities, e.g. 2 ppmw of total impurities would then be 5N2 [1]. With 40%, see Figure 1, they take the biggest share in the annual tellurium consumption [3]. Owing to its low electronegativity, tellurium forms materials with small bandgaps that can be addressed by relatively long-wavelength light [4]. The high absorption coefficient of CdTe enables the solar cells to capture the majority of the incident solar radiation in a thin layer [5].

When tellurium is alloyed with cadmium and mercury, a compound is formed that serves as an excellent infrared detector. In an alloy with zinc, tellurium makes a good gamma ray detector [6]. Another widespread use of tellurium is in thermoelectric cooling and heating devices. Compounds of tellurium with

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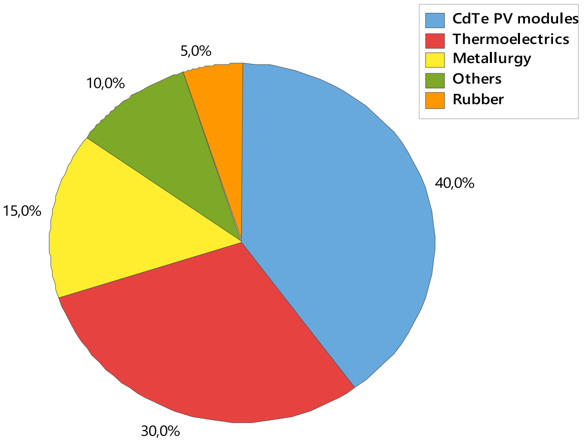

**Figure 1.** Main applications of Tellurium [2].

bismuth, selenium and antimony are used in certain electronic and thermoelectric applications, because of their superior efficiency in e.g. recovery of waste heat from 300 up to 473 K [7].

Other applications of tellurium include alloying additive in free-machining steels and copper to enhance mechanical properties like machinability, ductility and tensile strength without reducing the conductivity [8]. In addition, tellurium-based alloys are not affected by the corrosive action of sulphuric acid. Tellurium is also present in cast iron alloys, optimising the temperature control. Likewise, it is added to improve corrosion, vibration and fatigue resistance as well as mechanical properties [6].

Tellurium fulfils a series of other applications too. Tellurium chlorides, for example, are used as metal coatings give silverware a durable and attractive black antique colour. The addition of tellurium to glass and ceramics also provides blue to brown colours. It could furthermore be used as lubricants. As tellurides of refractory metals such as zirconium and titanium are heat and vacuum/stable, they demonstrate their uses in self-lubricating composites in electronics and aerospace fields. Other applications include detonators and initiators that are used in radical polymerisation reactions or as gasoline additive in automobiles [8]. Last but not least, tellurium, representing 5% of the demand, is used as a catalyst in organic chemical industry for synthetic fibre production and in the vulcanisation of rubber [9].

### *1.2. Tellurium's sources. Worldwide production and prices*

For primary sources, it is estimated that 1000 tons of copper sulphide ore contain about 1 kg of tellurium. In the line processes of copper extraction, tellurium is distributed along copper or dispersed over waste and dust. To obtain copper cathodes, copper anodes are electrolytically refined, resulting in a solid deposit of insoluble impurities at the bottom of the electrolytic tank, called anode sludge. Other options, such as bismuth telluride, gold telluride, and lead/zinc ores, can be considered as potential sources of tellurium too [6]. A total of 16,000 t of resources is estimated from countries, for which no individual data are available, followed by other global resources in China with 6600 t, Peru with 3600 t and the U.S.A. with 3500 t [4,9]. Figure 2 illustrates the price of tellurium in the U.S.A. in relationship with the worldwide refinery production.

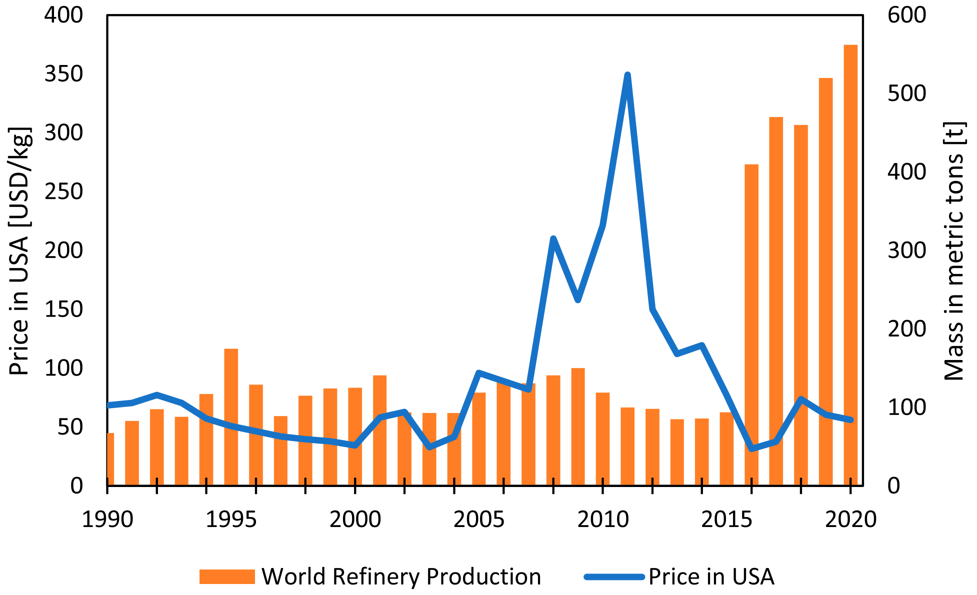

**Figure 2.** Tellurium price development in U.S.A. and the global refinery production, sourced from [10,11].

In 2017 worldwide production was estimated to be at least 420t, and the main producers were China (280t), Sweden (40t) and Japan (38t) [6]. According to Figure 2 and the price reports released by USGS [4,9], the value of tellurium reached his highest level (349 US$/kg) in 2011 within the last thirty years. In the following six years, the price of tellurium decreased to 20% of its previous peak.

A further summary on the world production and consumer applications of tellurium has been summarised by Mahmoudi [12] for the year 2019 as seen in Figure 3.

### 1.3. Problems arising from commercial application

Cadmium-telluride thin-film solar cells are relatively easy to manufacture, which is why their commercialisation is progressing the fastest compared to other thin-film solar cells. It has moved from the laboratory research stage to large-scale industrial production. The next step in the research and development of CdTe solar cells is to further reduce costs, increase efficiency, and improve and perfect the production process [13]. At present, the market share of CdTe cells is not satisfactory, and the reasons for its inability to rise to the mainstream of the market include the following:

First, the cost of modules and substrate materials is too high. The overall CdTe solar cell materials account for 53% of the total cost, while semiconductor materials account for only 5.5%. Second, natural tellurium deposits are limited, and the total amount of tellurium will not be enough to cope with the large number and overall dependence on such photovoltaic cells for power generation. Third, the toxicity of cadmium makes it impossible for people to accept such photovoltaic cells with confidence. Regarding CdTe solar cells, as a large-scale production and application of photovoltaic devices, the environmental issues should not be ignored. The pollution of the environment by the toxic element cadmium (Cd) and the health risks to users cannot be underestimated. We cannot obtain clean energy and at the same time cause new hazards to human body and human living environment. It is not technically difficult to effectively dispose of discarded and broken CdTe components. However, cadmium is a highly toxic heavy metal, and its compounds are toxic as well [13].

Cadmium harms humans and animals by Cd-containing dust in the respiratory tract, and ecological pollution is caused by discharging of wastewater. Therefore, Cd and Te on broken glass should be removed and recycled, damaged and discarded components should be properly disposed, as well as wastewater and waste discharged from production should be treated in accordance with environmental standards. At present, all countries are committed to solving the factors that restrict the development of CdTe thin-film solar cells, and it can be expected that the above problems will be solved one by one, so that CdTe thin-film cells can become one of the new energy components of society in the future [13].

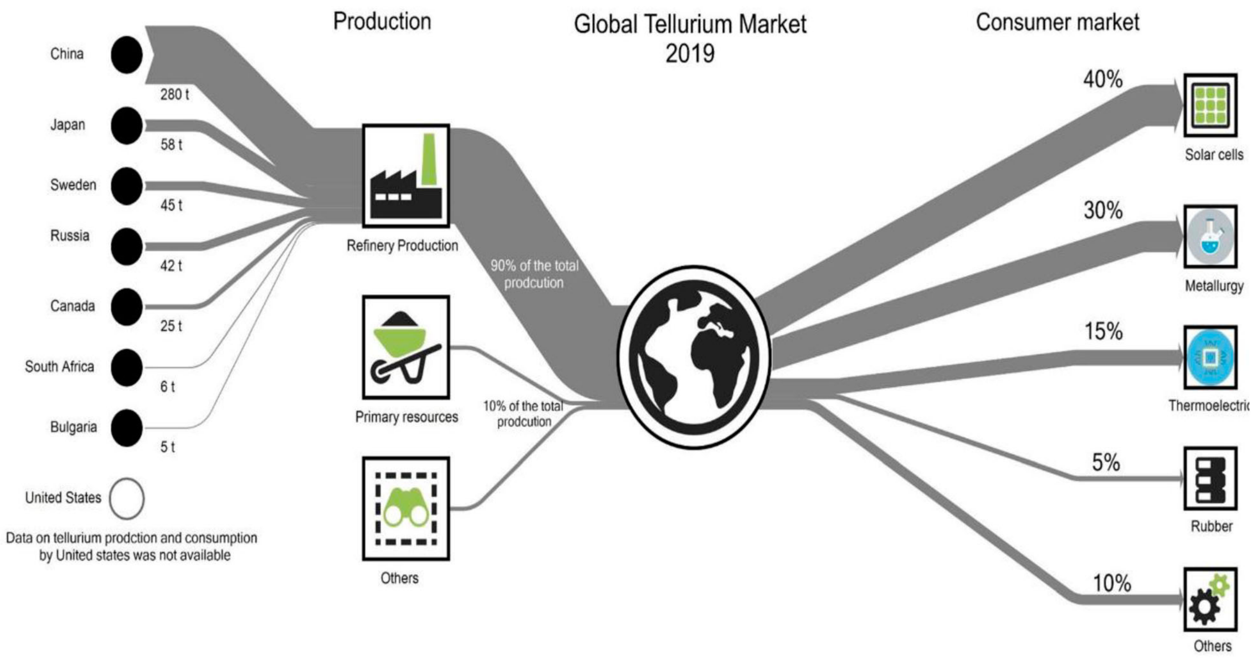

**Figure 3.** World production of tellurium and consumption as adapted from [12].

## 2. Production of commercial grade tellurium

### 2.1. Tellurium recovery processes through primary source

As stated earlier, tellurium is mainly produced during the electro-refining process of copper, obtained in the form of tellurium dioxide or metallic tellurium through extraction from anode sludge [14]. The copper anodes after fire-refining process contain the highest tellurium concentration within the distribution route (see Table 1). Then, the anodes are treated by electrolytic refining with a copper sulphate solution where the copper anodes dissolve in the solution in form of $Cu^{2+}$ cations, then migrates and deposits on the cathode to form copper cathodes. During the dissolving of copper anodes, metallic impurities such as Au, Ag, Pt, Se, Te, Pb, Sn remained undissolved and precipitates, e.g. in the form of PM selenides or tellurides, to the bottom of the tank, forming a sludge or slurry. Some impurities such as Bi, Fe, Co and Ni would remain in the electrolyte. Regarding tellurium, more than 98% of it contained in the anode is insoluble in the copper sulphate solution, precipitating in the sludge. Therefore, copper sludge is an excellent starting material for the recovery of gold, silver and platinum group metals.

A minimal amount is now recovered by recycling PV solar cells. Tellurium is usually present in copper ores as metal tellurides such as copper telluride ($Cu_2Te$) and as noble metal tellurides such as hessite ($Ag_2Te$) and calaverite ($AuTe_2$) [18]. Some other copper sulphite minerals also contain certain amount of tellurium, ranging from 0.04 ppmw up to 600 ppmw. A table compiled by Moats et al. using data from [19,20,21,22] has been adapted for this review, focusing only on the tellurium content (compare Table 2). This demonstrates the dependency of tellurium's availability towards the amount of copper production, as tellurium are often byproducts of it. Nassar et al. [17] have reported the locations and amount of copper cathode production extensively. From there on, the authors calculated the potential amount of tellurium, roughly a potential of 1900 metric tons in the year 2018. This takes into account the different concentration of tellurium and some other impurities in the sludge and other copper material, which varies significantly depending on the initial ore.

Several extraction methods and processes displayed for tellurium from anode sludge have been examined so far [18,23,24,25]. Throughout the world, many different facilities treat copper anode sludge to recover Te with different methods, some of these facilities are summarised in Table 3 according to [26,27,12]. Additionally, other companies reported to produce tellurium or tellurium products are listed in Table 4.

Both pyrometallurgical and hydrometallurgical processes are known for the treatment of copper anode sludge after copper electrolysis [8,25,36,37]. According to CCR Canadian Copper Refinery, the main

**Table 1.** Distribution of tellurium in copper material [15–17].

| Material | Amount of Te in wt.% |
|---|---|
| Copper Concentrate | 0.001–0.0024 |
| Copper sulphide concentrates | 0.0015–0.005 |
| Copper matte | 0.0011–0.0018 |
| Crude copper | 0.0025–0.004 |
| Anode copper | 0.0076–0.0143 |

**Table 2.** Reported concentrations of tellurium in sulphite minerals, adapted from [16].

| Mineral | Tellurium Content in ppmw |
|---|---|
| Chalcopyrite ($CuFeS_2$) | 0.04–300 |
| Bornite ($Cu_5FeS_4$) | 27.4–148 |
| Pyrite ($FeS_2$) | 26.3–600 |

**Table 3.** Copper Anode Sludge Treatment around the globe adapted from [12] according to [26,27].

| Facilities (Countries) | Treatment |
|---|---|
| CCR (Canada) | Removal of Cu and Te from sludge through acidic oxidative leaching. |
| INER (China) | A complete hydrometallurgical process recovers Au, Ag, Te, Se, Pb, Cu and Sn. |
| Aurubis AG (Germany) [28] | Separation of Cu and Te from the sludge through aeration acidic leaching. Te is recovered by cementation with Cu shots. |
| Sarcheshmeh (Iran) | Cu removal from the sludge by re-pulping the anode sludge in the spent electrolyte. Te can be then found in the residue. |
| NML (India) | Te dissolved by atmospheric acidic leaching in presence of oxidant and NaCl. Te then separated and recovered via solvent extraction. |
| India Copper Complex (India) | Te is removed from the sludge through a two-stage-acidic leaching. |
| Hitachi Smelter (Japan) | Te and Cu removal by leaching with ferric sulphate. |
| Sagoneoseki (Japan) | Anode sludge first re-pulped into electrolyte. Cu and Te are removed by purging air, and then recovered as $Cu_2Te$. |
| GrupoMexico (Mexico) [29] | Production of selenium and tellurium in the Precious Metals Plant from copper anode sludge. |
| Nornickel, Norilsk Division (Russia) [30] | Production of tellurium along other platinum group metals (PGM) from the precious metal concentrate coming from the copper refining. |
| Umicore (Belgium) [31] | Recovery of tellurium from anode sludge. |
| Boliden AB (Sweden) [32] | Copper telluride by products from the treatment of anode sludge in the precious metal recovery. |
| Asarco LLC (USA) [2] | Semi-refined tellurium from copper anode sludge, exported to Mexico for further processing. |
| Freeport-McMoRan Inc (USA) [6] | Semi-refined tellurium from copper anode sludge, exported to Asia for further processing. |

**Table 4.** Examples of companies producing tellurium from non-copper anode sludge materials.

| Companies (Countries) | Products (Welche Wege) |
|---|---|
| First Tellurium- Klondike and Deer Horn [33,34] (USA) | Production of tellurium from gold-tellurium mine |
| Boliden AB (Sweden) [35] | Tellurium production from gold-tellurium mine. |
| Umicore (Belgium) [31] | Production scrap from $Bi_2Te_3$ manufacturing and defective end-of-life solar panels |

components of copper anode sludge they produced are Cu (10–50%), Ag (3–25%), Pb (5–10%) and Se (2–15%), while Tellurium is in range of 0.5–8% [38]. There are three methods for tellurium recovery based on hydrometallurgical treatment: (i) pressure leaching in an alkaline solution or (ii) with sulphuric acid, or (iii) aeration leaching also with sulphuric acid. Then, there are a series of pyrometallurgical processes that continue the tellurium extraction. These include oxidation roasting, soda ash roasting, soda ash smelting, cupellation and, finally, sulphating roasting. In these various sludge treatment technologies, copper, selenium and tellurium are usually removed first, and then processed to the recovery of gold, silver and platinum group metals [8]. It is worth mentioning that in the majority of the processes for the recovery of valuable metals from anode sludge, tellurium was left aside as an unimportant metal by cooper smelters [25]. This could be associated with the low level of tellurium content and its high volatility, which do not sync well with the demand and price of tellurium.

Current practices agreed that copper in anode sludge must be removed by acidic pressure leaching with sulphuric acid [39], which eventually became the predominant leaching process for decoupling in sludge treatment [18]. In this step, seen in Figure 4, the copper is removed by oxidative pressure-leaching with dilute sulphuric acid at high temperature (80–160°C), which leads to almost complete copper extraction as well as the tellurium extraction of 50 to 80% [36]. Nonetheless, this process should be able to obtain the greatest quantity of tellurium (>90%), without dissolving selenium and/or silver [23]. Upon filtration to remove the de-tellurised sludge, cementation with copper is performed to extract tellurium from solution. The copper telluride is recovered in a relatively pure state, which is then mixed with sodium hydroxide (NaOH) and air to form sodium tellurite solution ($Na_2TeO_3$ +$H_2$) and basic copper salts. The resulting sodium tellurite solution enables the possibility of further processing through electrowinning to deposit metallic tellurium on the cathode [40]. The cathodic and anodic reaction for the electrowinning of Te was reported by Fan et al. [41]:

$$\text{Cathode}: TeO^{2-}_{3(aq)} + 3H_2O_{(l)} + 4\,e^- \rightarrow Te_{(s)} + 6OH^-_{(aq)} \tag{1}$$

$$\text{Anode}: 4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4\,e^- \tag{2}$$

An alternative route for treating the anode sludge is via soda ash roasting. The anode sludge is first mixed with sodium carbonate ($Na_2CO_3$) at temperatures above 500°C under atmospheric gas. Precious metals such as Ag and Au are reduced to elemental metals from $Ag_2Te$ and $Au_2Te$, while the telluride anions are oxidised to $Na_2TeO_3$ (compare Equation 3). The resulting $Na_2TeO_3$ is then dissolved in water, where it undergoes a basic reaction to form hydrogentellurate ions ($HTeO_3^-$). By addition of sulphuric acid, tellurium dioxide ($TeO_2$) precipitates in water (compare Equation 4). Metallic tellurium can be obtained from $TeO_2$ either by the chemical way of reacting with $SO_2$ inside mineral acids or through leaching and subsequently electrolysis. [42]

$$Cu_2Te + O_2 + Na_2CO_3 \rightarrow Na_2TeO_3 + 2Cu + CO_2 \tag{3}$$

$$HTeO_3^- + H_2SO_4 \rightarrow TeO_2 + SO_4^{2-} + H_2O \tag{4}$$

$$TeO_2 + 2SO_2 \rightarrow Te + 2SO_4^{2-} + 4H^+ \tag{5}$$

Considering the efficiency parameters of the aforementioned processes, the maximum theoretical yield of 100% can be reached by acid aeration, followed by alkaline pressure 99.9%, and in third place acid pressure >90%. These numbers solely describe the leaching efficiency; however, some studies have reported 80% yield as a reasonable upper limit for tellurium extraction from copper anode sludge [36]. Therefore, the average recovery of tellurium varies between 70 and 80% [43].

## 2.2. Alternative tellurium recovery processes

The methods mentioned in chapter 2.1 both require a tellurium electrowinning step to obtain metallic tellurium. The combination of electrolysis, leaching and precipitations suffer from the high consumption of acids and generates large amounts of hazardous wastes. For a more efficient and economical recovery process, alternative processes have been investigated.

Li et al. [44] and the team from Kunming University of Science and Technology published a study in an attempt to recover Te from industrial copper telluride intermediate product provided by a local copper smelter. This copper telluride is produced in the comprehensive recovery of copper anode sludge, where the sludge goes through filtration, high-pressure acid leaching and eventual copper

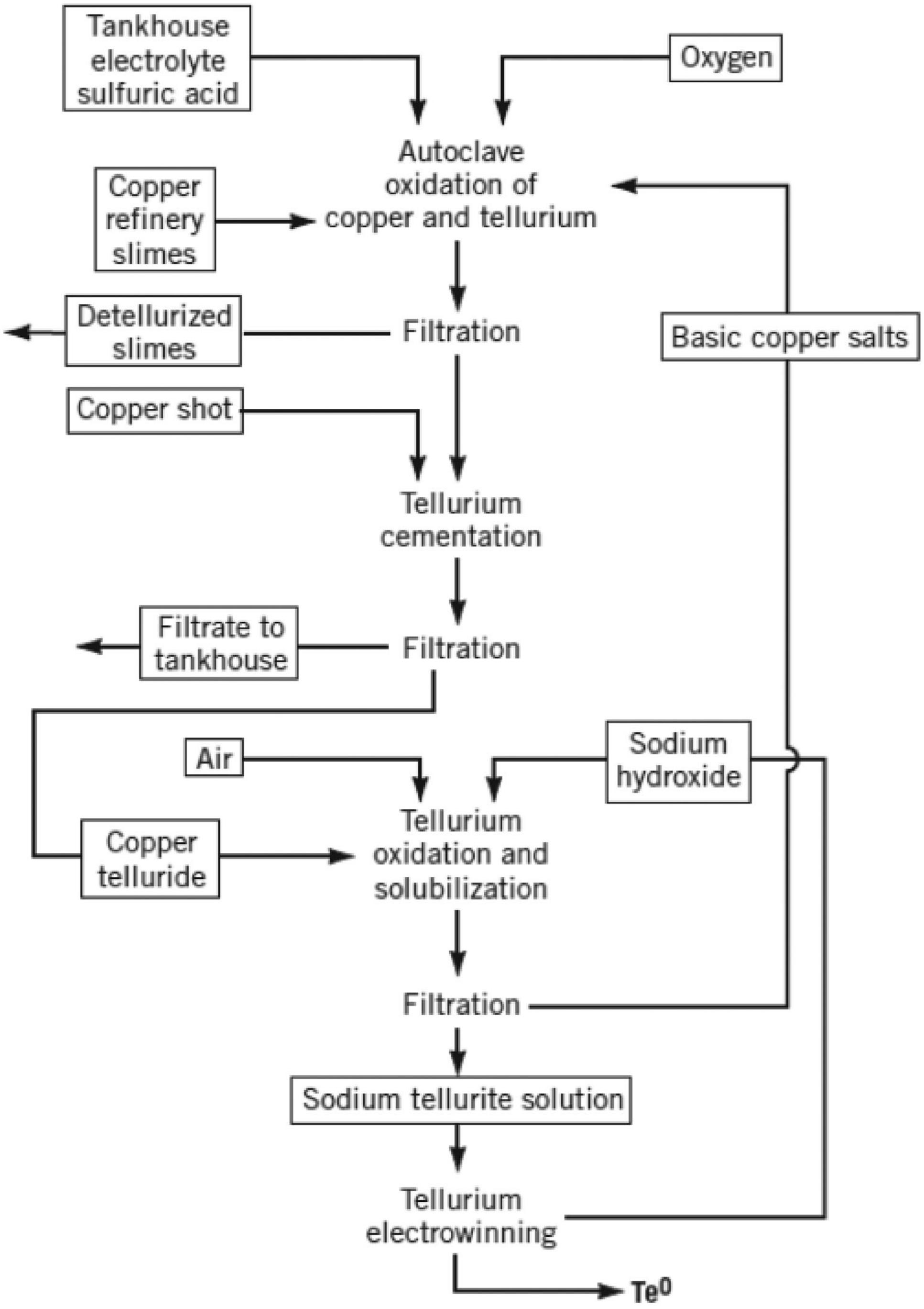

**Figure 4.** Flow sheet of hydrometallurgical route for tellurium extraction [25].

cementation, similar to the process mentioned in chapter 2.1. The chemical composition of copper telluride is shown in Table 5. The researchers combined three different processes to process the copper telluride into metallic Te. These processes include soda ash melting, neutral leaching and acid precipitation, and vacuum carbon thermal reduction (see Figure 5). The melting process was reported to yield 98.1% Te at 4 h of holding time at 1273 K. The leaching and precipitation yielded 99.08% of the Te into $TeO_2$ of 83.54% purity. In the reduction of $TeO_2$, metallic Te of 99.83% purity and yield of 96.85% was achieved after 60 min holding in the ideal

**Table 5.** Chemical composition of copper telluride measured by atomic absorption.

| Elements | Cu | Te | Se | Au | Ag | Ni | Sb | Bi |
|---|---|---|---|---|---|---|---|---|
| Content | 40.93 wt.% | 19.62 wt.% | 2.81 wt.% | 0.28 g/t | 116 g/t | 260 g/t | < 50 g/t | < 50 g/t |

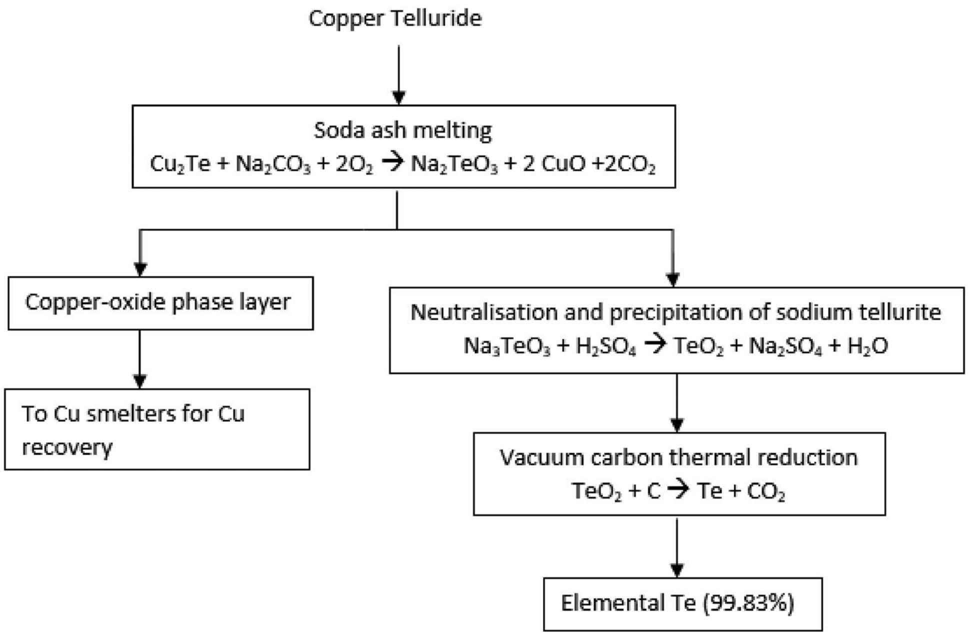

**Figure 5.** Adapted process route for the recovery of Te from industrial copper telluride intermediate product reported in the study of Li et al. [44].

experimental conditions of 873 K with a system pressure of 10–20 Pa. All in all, the study reported here manages to recover metallic Te close to commercial purity with a very robust combination of hydro- and pyrometallurgy.

Alternatively, another process flow for extracting Te out of a similar copper telluride that Li et al. used [44] was reported by Shen et al. [37] as seen in Figure 6. This was provided by Tongling Nonferrous Metals

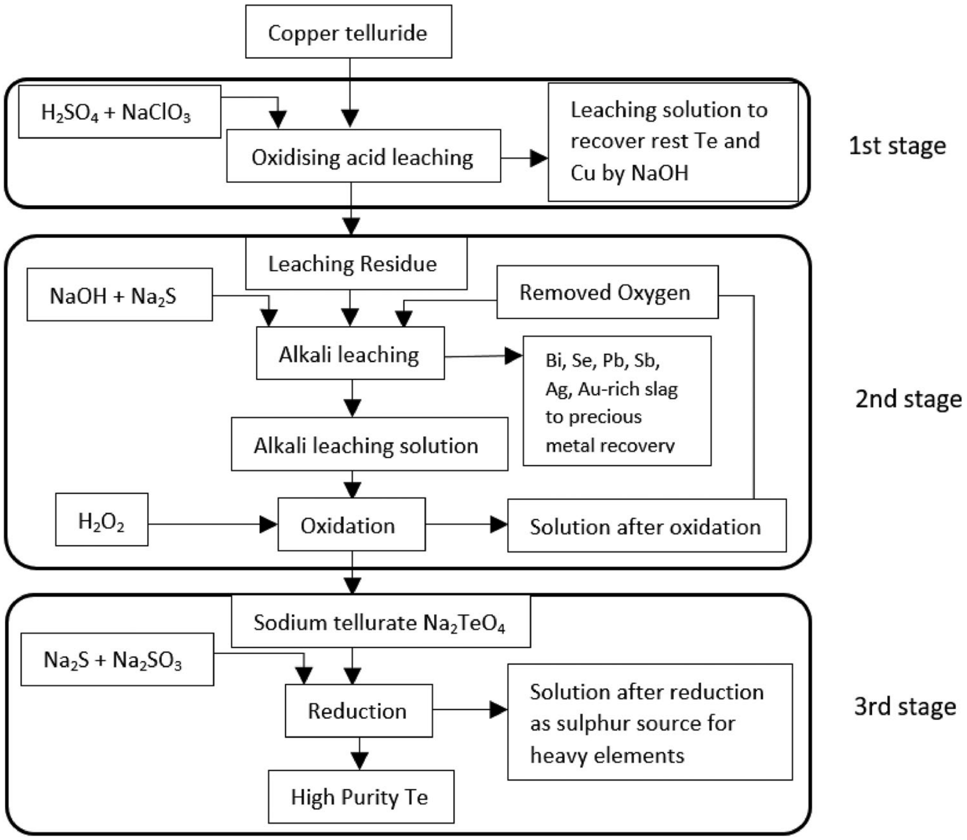

**Figure 6.** Flow sheet for extracting Te from copper telluride, edited from [37].

Smelter in China, whose chemical composition of this material is included in Table 6. In the first stage, Cu removal efficiency sums up to 99.44%, leaving the Te in the residue. This residue is leached in the second stage, with leaching efficiency up to 99.58%. During this stage, the removal of the main impurities in Te such as Bi, Pb, Sb can be achieved by the addition of $Na_2S$. Precipitation of $Na_2TeO_4$ by addition of $H_2O_2$ to the alkaline leaching solution leaves Se within the solution. Through $Na_2S$ and $Na_2SO_3$ reduction, metallic Te powder up to 99.98% was obtained. Along with this high purity comes the high extracting efficiency of 96.18%.

### 2.3. Tellurium recovery process through secondary resources

The discussion on Te recovery through secondary sources could be traced back to its applications mentioned in section 1, where photovoltaic modules, thermoelectric materials and metallurgy delivers the main raw materials for Te recycling.

A material for Te's recycling is CdTe solar cells, as it has recently been produced on a large scale and, for which a recycling process has been developed [45]. Te has been removed from the EPA* hazardous waste list due to its insolubility in water [46]. Therefore, in the United States, CdTe photovoltaic modules that meet the leaching criteria of reducing the Cd content to lower than 1 mg/L [47], can be disposed in commercial landfill as non-hazardous waste. Nevertheless, the continuous efforts are focused on the recycling technologies, despite high economic costs. In 2011 the United Nations Environment Programme (UNEP) [48] reported the global end-of-life recycling ratio of tellurium estimated to be <1%. The current forecast for CdTe industry is that tellurium supply could be entirely dependent on recycling process modules by 2038 [49]. (*) United States Environmental Protection Agency.

The recovery of tellurium via hydrometallurgical route can be done by acid dissolution and subsequent precipitation in alkaline environment. According to Zhang et al. [50], the two main chemical equations for recovering Te from the CdTe are listed below:

$$CdTe_{(s)} + 3H_2SO_4 + 3H_2O_2 \rightarrow CdSO_{4(aq)} + Te(SO_4)_{2(aq)} + 6H_2O \qquad (6)$$

$$Te(SO_4)_{2(aq)} + 2Na_2CO_{3(s)} \rightarrow TeO_{2(s)} + 2Na_2SO_{4(aq)} + CO_2 \qquad (7)$$

According to the authors, the $TeO_2$ can be reduced by hydrogen to obtain metallic Te directly, or can be dissolved in a NaOH or KOH solution, producing $K_2TeO_3$. This compound could then be used to produce tellurium ingots via electrolysis. Other approaches are such as recovery of CdTe by ammonia precipitation instead of $Na_2CO_3$ [51], Zn or Fe precipitation [50], the application of ion exchanger [40,52], direct electrolysis using electrolyte solution to dissolve CdTe [53].

Investigation on recycling CdTe photovoltaic modules is concerned with optimising the segregation and recovery of their components (glass, cadmium and tellurium) with the lowest possible impact in terms of emissions, energy and economic efficiency (low cost). Some patented technologies allow the recovery of tellurium from spent photovoltaic cells by crushing the photovoltaic devices, followed by a hydrometallurgical- (leaching) [54,55] or pyrometallurgical process (pyrolysis) [43]. In the industry, First Solar's recycling facility recycles over 90% of the semiconductor material and 90% of the glass material using current process technology for low-cost reuse, as the recycling concept is fully integrated into the module design [45]. This technology includes the shredder, hammer mill, and film removal operations from the modules, followed by solid/liquid separation, precipitation and dewatering steps to obtain CdTe filter cake [56].

Regarding the availability of secondary raw materials, in future, the accumulated global production of CdTe PV modules is estimated to be 0.9–1.8 $TW_p$ (Tera Watt-peak) by 2050 as well as 3.8–10 $TW_p$ by 2100 in comparison to 120 $GW_p$ by 2020 [57]. A rough conversion of the amount from $TW_p$ to tonnage mass was reported in [23], such that 1 TW needs 90,000 t of Te. Recycling of PV modules at the end of their effective life-time (20–25 years) will close the life-cycle of production of CdTe solar cells and solves drastically the environmental issues, and create a secondary resource of tellurium.

Another secondary source of materials for tellurium recycling are thermoelectric materials or sometimes referred to as thermoelectric generators. Three types of thermoelectric material were compiled by Casteneda et al. [58], including $Bi_2Te_3$ p-type, $Bi_2Te_3$ n-type, and

**Table 6.** Chemical composition of copper telluride intermediate product measured by X-ray fluorescence (XRF).

| Elements | Cu | Te | Se | Au | Ag | As | Sb | Bi |
|---|---|---|---|---|---|---|---|---|
| Content | 37.65 wt.% | 38.85 wt.% | 0.09 wt.% | 1.13 g/t | 105 g/t | 2.19 wt.% | 0.31 wt.% | 5.47 wt.% |

PbTe-SrTe. The published results on the recycling of thermoelectric materials are relatively underdeveloped compared to photovoltaics materials at the time this review was being written. Although only a small fraction of the thermoelectric materials, or semiconductor components are recycled, some methods for recycling of Tellurium from $Bi_2Te_3$ based on different chemical, thermal and microbiological separation processes were reported [59]. The separation of components from commercial modules containing plastics, Cu, $Bi_2Te_3$ and $Al_2O_3$ can be achieved by mechanical processing and sorting technologies.

This type of separation begins with thermal treatments such as a hot oil bath at 250°C to separate n-type $Bi_2Te_3$ and the p-type $Bi_{0.5}Sb_{1.5}Te_3$ from the solder. Subsequent treatment with aqua regia precipitates the Sb, leaving nano-powders of $Bi_2Te_3$ remaining [60,61]. Direct recovery of metallic tellurium from spent $Bi_2Te_3$ was reported by Sasai et al. [62], who placed $Bi_2Te_3$ powder into $H_2SO_4$, heated it up to 200°C and held for up to 20 h. The hydrothermal treatment was intended to oxidise the $Te^{2-}$ in the $Bi_2Te_3$ to form metallic Te. A Korean group utilised the dissolving characteristics of Te in acidic solution and examined the recyclability by using solvent extraction test with tributyl phosphate as the organic phase, effectively separating Te from $Bi_2Te_3$ and $Sb_2Te_3$ in the acid solution [63,64]. Chinese metallurgists used vacuum distillation method on $Bi_2Te_3$ scraps and managed to purify Te from 41.53% to 98.88%, supplemented with a thorough theoretical analysis of the distillation rate, separation coefficient and the effect of distillation temperature [65].

A comprehensive review on the recovery of Te from metallurgical intermediates and E-waste was published [66], discussing several traditional and novel methods. However, no other literature described the recovery of tellurium from $Bi_2Te_3$ or PbTe. Furthermore, the discussion of recycling Te up to high purity are falling far behind other metals such as Cu and Al. The lack of information and literature on this topic provides an excellent outlook to bridge the gap between waste products to metallic tellurium, which could then be purified for further applications in solar- as well as thermoelectric modules.

## 3. Production of high- and ultrahigh purity Te

The purification of tellurium has been widely reported since its intensive development and use in semiconductor devices. The required minimum purity of the starting material for tellurium-based II-VI compound semiconductors is 6N grade. This purity is mandatory for high-performance fabrication and is being increased to 7N purity level due to the demand for better devices. For optoelectronic applications e.g. the 7N grade with minimum gaseous and gas-forming impurities is demanded [67].

Most processes for the recovery of ultra-high purity metals (UHP, above 6N) are generally based on physical mechanisms. The most commonly used non-chemical methods for purifying tellurium are vacuum distillation followed by horizontal zone melting for further refining. Only few studies have been published on chemical methods to obtain a 5N-Te from tellurium-containing crude copper and/or selenium [68]. Also, high-purity tellurium has been once achieved through plasma-assisted chemical transport reaction with hydrogen to form $H_2Te$ followed by thermal decomposition [69].

After recovery from anode sludge, the tellurium product has a commercial grade of 99.7–99.99%, including the impurities of copper, silicon, selenium, lead, iron, arsenic and bismuth [27,70]. In most cases, these impurities can be reduced to ppmw levels by vacuum distillation. Vacuum distillation has been successfully demonstrated to increase the tellurium purity levels from 99.97% to 99.999% [71–75]. In addition, it is possible to achieve higher purity of tellurium when hydrogen atmosphere is included in the system [24]. In this process, experimental conditions and process parameters for molten, evaporated, and condensed phases must be well established to optimise the results. These parameters include, but are not limited to, the evaporation rate (as a function of T, P, and the size of the surface, on which evaporation can occur), the composition of the material on the surface and the initial content of impurities in the feedstock.

After that and to eliminate or reduce the content of remaining impurities, the well-established method to attain >6N-Te purity levels is zone refining [12,76]. Zone refining is the process generally used to transition from 4N to 6-7N through various steps/passes [77]. In this method, the operating conditions, such as moving velocity of the zone, molten zone length, as well as zone temperature are decisive.

### 3.1. Vacuum distillation of tellurium

Without going into the details of the principle of vacuum distillation, this method is worth applying when there is a significant difference between vapour pressures of different substances in a material. The so-called Antoine equation; i.e.

$$\log_{10}(P) = A + B/(T + C) \qquad (8)$$

whose coefficients have been compared by Yaws [78] for tellurium and several other elements at 500°C as shown in Figure 7, obviously exhibits that the elements Zn, Na,

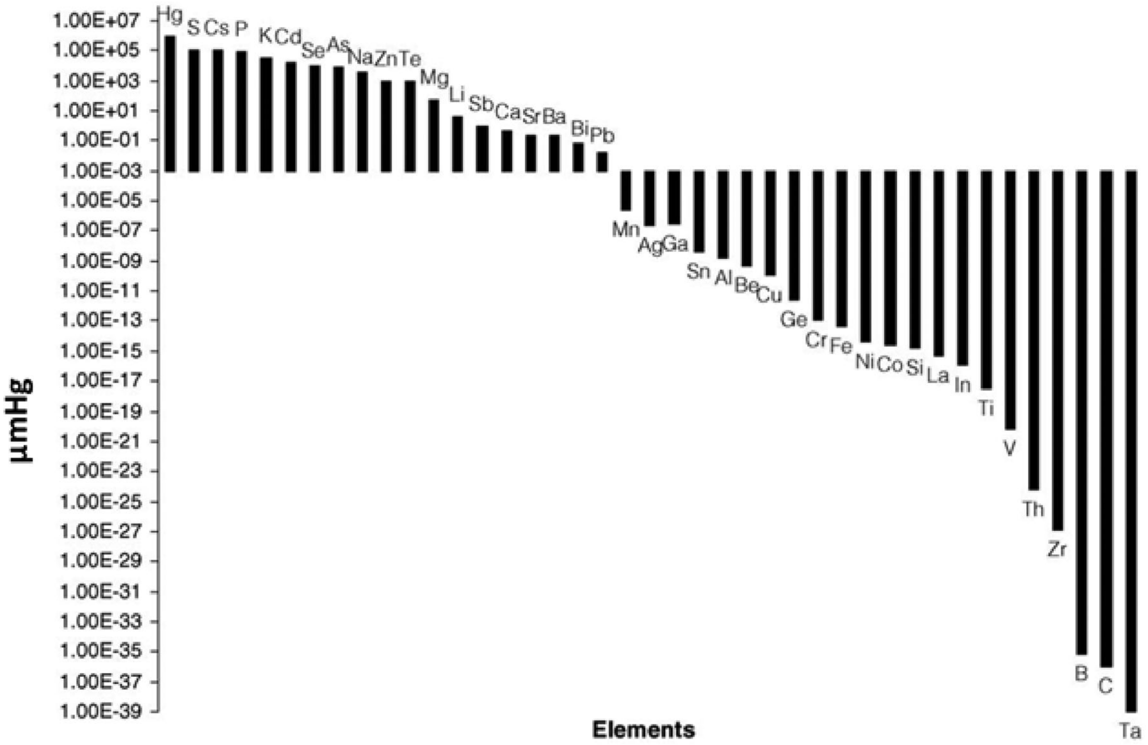

**Figure 7.** Vapour pressure in μmHg of various substances at 500°C [73].

Cd, K, Se, As, among other elements have a higher vapour pressure than tellurium. Therefore, they are expected to evaporate before tellurium, while a larger number of other elements with lower saturated vapour pressure remain in the residual after the process concludes. Nevertheless, the Antoine equation disregards the solutes and elements with activities lower than one, serving only as a first impression from the refining feasibility point of view. Hence, this rough comparison does not take the interactions of a multi-component system into account.

With the aim of achieving a more accurate estimation of the separation ability and quantifying it, the separation coefficient β for a binary or multicomponent system during vacuum distillation can be used [79]. This parameter considers the interaction of the elements forming a binary system and allows measuring the degree of segregation based on thermodynamic equilibrium principles. The expression of β for a binary i-j alloy was derived as $\beta = (\gamma_i/\gamma_j) \cdot (P_i^*/P_j^*)$, where $\gamma_i$ and $\gamma_j$ are activity coefficient for i and j components; $P_i^*$ and $P_j^*$ are saturated vapour pressure of pure elements for i and j, respectively. The criterion for the separation to occur is that the β-values must be much larger or much smaller than unity.

In the extensive literatures, high-purity tellurium is obtained exclusively by vacuum distillation in single- and/or multi-stage stages. The highest efficiency was achieved by a starting material of 4N + to the final purity level of 6N-Te [71]. Prasad et al. [72] and Potolokov [80] investigated the purification of 3N-tellurium by a two-stage vacuum distillation gaining 5N- as well as 6N-grade products, without information on Selenium and Cadmium concentrations. In Figure 8, the schematic for a vacuum distillation has been illustrated by Prasad et al. [71] and Wedlock. The Figure 8 (right) however, shows a special design apparatus, which allows a single run of a three-zone distillation process, using dynamic vacuum of about $5 \times 10^{-3}$ Torr.

### *3.1.1. Selenium and other impurities*

Selenium is the principal impurity, which is very difficult to reduce by vacuum distillation, as the optimum condensing temperature of Se is very similar to that of Te at near vacuum pressure i.e. 0.005 Torr as reported [72,73]. In addition to that, despite the fact that at all temperatures, the saturated vapour pressure of Se is higher than Te, the difference between the two elements is low [82] (compare Figure 7). Therefore, the removal of selenium is not viable and has to be attained by the reaction with hydrogen during vacuum distillation [24]. This can be accomplished either by injection/bubbling hydrogen gas into liquid tellurium, or by using a dynamic hydrogen ambient, in both

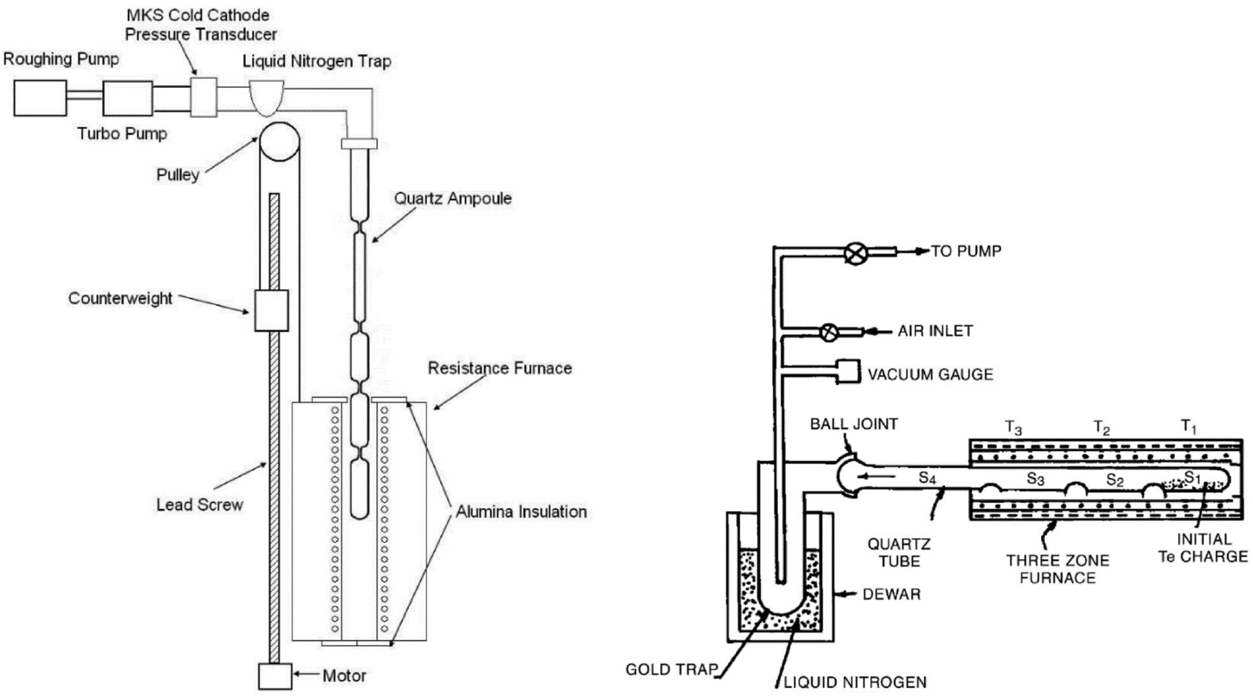

**Figure 8.** Schematic of tellurium distillation system [71] (left) and Schematic for triple distillation apparatus in single-run. [73] [81] (right).

cases produces $H_2Se$ [83] gas according to the following equation and is then transported to the surface of the melt [84]:

$$Se_{(l)} + H_{2(gs)} \rightarrow H_2Se_{(gas)} \tag{9}$$

During distillation, impurities with lower vapour pressure than that of Te, such as Ca, Bi, Pb, Mn, Ag, Sn, Al, Fe, and Ni tend to remain in the melt [85]. Other impurities such as Sb, Mg, Zn, Na, As and Cd are very close to or higher than that of Te at 500°C. These elements are therefore difficult to be removed by distillation. But, in the report by Zaiour et al. [86], it was stated that volatile impurities such Ca, Li, K, P and S can be removed from tellurium melt by purging inert gas to increase the pressure within the medium. However, this result contradicts the vapour pressure difference theory mentioned above, as Ca and Li have lower vapour pressure, while K, P and S have higher vapour pressure than Te. Zaiour et al. explained this observation by relating the vapour pressure to the initial concentrations of the feedstock.

### 3.2. Zone refining of tellurium

Zone refining is the most efficient process employed for tellurium purification to achieve purity grade higher than 5N, about which various studies have been reported. Munirathnam et al. [67] reported that a 3N-Te raw material was purified in a graphite crucible under vacuum of nearly $1 \times 10^{-5}$ Torr at about 800 K and subsequently with zone melting in a quartz boat under a continuous flow of $H_2$ gas. The result was 7N ultrapure tellurium with combined content of carbon, nitrogen and oxygen to be 208 ppbw, silicon impurity at 50 ppbw and other elemental impurities below detection limits of GDMS (Glow discharge mass spectrometry).

Pfann [77] introduced the uniqueness of the zone melting technology in 1952, which is like other fractional crystallisation techniques, based on the concentration difference of an element in the liquid to that in the solid form of a substrate. This parameter is named distribution coefficient and defined for every impurity as $k = C_s/C_l$ . When a k-value far from unity, the separation of the respected impurity via zone refining can be well succeeded, while for the impurities with $k \approx 1$, it is almost impossible. Zone refining generally purifies a metallic element or compound by melting a short region (i.e. zone) and causing this molten zone to travel extremely slowly along a long solid ingot. While this zone travels, it redistributes impurities along the charge, brings those with $k << 1$ always to the end of the ingot, in accompanying with the moving molten zone. After many passes of the process, the most purified part of the ingot then remains in the solidified area at the beginning of the ingot. Figure 9 illustrates a simple sketch of a one-heater zone melting as well as solute concentration

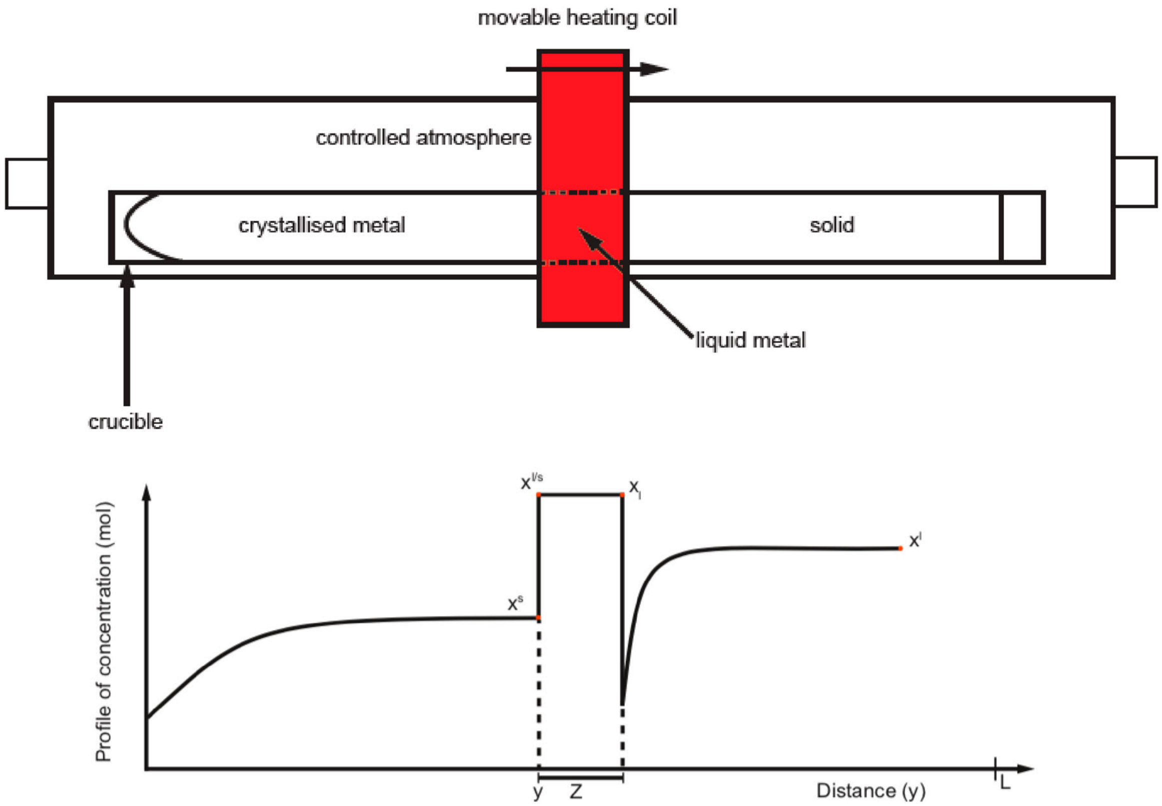

**Figure 9.** (Top) Scheme of zone refining with one heater and (Bottom) solute distribution along the bar in case of complete mixing in the molten zone owing to convection [87].

distribution along the bar. The temperature during the process is set in most cases around 753-773 K. It was found that higher temperatures of the molten zone will increase the segregation coefficients and at the same time decrease the effective diffusion coefficients ($D_{eff}$) and therefore the capability of purification is reduced [88,89].

### 3.2.1. Distribution coefficient of impurities in tellurium

As mentioned above, the estimation of purification efficiency via fractional crystallisation is given by the term of distribution coefficient. However, the purity of tellurium is dependent not only on the theoretical distribution coefficient k, coming from the binary phase diagrams and considering the equilibrium, but also, to a large extent, on the travel rate of the solid–liquid interface and the diffusion rate of the solute in the liquid. Burton, Prim and Slichter [90] reported this phenomenon in a so-called BPS model, introducing three physical parameters in the formulation; the growth rate of the solid, the diffusion of the impurity into the melt and the thickness of the diffusion boundary layer, as seen in the following:

$$k_{eff} = k_0/\{k_0 + (1 - k_0) \cdot \exp(-V\delta/D)\} \qquad (10)$$

where $k_{eff}$ is the effective segregation coefficient, V is the movement rate of a solid–liquid interface, δ is the boundary layer thickness, and D is the solute diffusion coefficient. If ideal condition is approached by experimental conditions, $k_{eff}$ value will be very close to the equilibrium distribution coefficient k. For a number of impurities in tellurium, the effective distribution coefficients ($k_{eff}$) have been experimentally determined during directional solidification processes (see Table 7), while equilibrium coefficient k can be calculated with thermodynamic modelling software like FactSage. In the available binary phase diagrams with tellurium, nearly 30 elements are found including Ag, Au, Cd, Cu, Fe, Ge, Hg, Pb, Sb, Se, Sn and Zn [95].

The presence of equilibrium or effective segregation data are not only established with pure elements, but there is also information available for intermetallic compounds of type $Te_nX_m$-Te which is relevant especially in case of doping treatment. The study from Kujawa [96] reported that almost without exception, phase diagrams of Te-X are characterised by multiple occurrences of $Te_nX_m$ and the corresponding number of eutectics with low mutual solid solubility of the components. Such intermetallic phase is normally formed under the presence of miscibility gap, in the case of $Te_nX_m$, they are normally found between eutectics. Only the Te-Se

**Table 7.** Reported effective distributions coefficients of various impurities contained in tellurium.

| Element | $k_{eff}$ | Element | $k_{eff}$ |
|---|---|---|---|
| Ag | $2 \times 10^{-4}$ [88], $2 \times 10^{-3}$ [89] 0.08 [91], 0.086 [80] | Mn | $5 \times 10^{-3}$ [89], 0.03 [88], 0.08 [80] |
| Al | 0.035 [91], 0.07 [86], 0.19 [80] | Mo | 0.16 [80] |
| As | $2 \times 10^{-4}$ [92], $9 \times 10^{-3}$ [89], | Ni | 0.04 [88], 0.58 [80] |
| Au | 0.002 [91] | Pb | 0.19 [89], 0.02 [88], 0.096 [80] |
| Bi | $4 \times 10^{-4}$ [92], 0.5 [93] | Pd | $7 \times 10^{-3}$ [88] |
| Ca | 0.01 [92], 0.28 [80] | S | 0.29 [92] |
| Cd | 0.26 [80] | Sb | 0.35 [93] |
| Cr | 0.05 [88], 0.24 [80], 0.25 [94] | Se | 0.44 [92], 0.48 [94], 0.58 [93] |
| Cu | $5 \times 10^{-3}$ [89], 0.011 [91], 0.23 [80] | Si | 0.15 [91] |
| Fe | 0.02, 0.05 [94], 0.26 [80] | Sn | $<10^{-3}$ [91], 0.22 [93] |
| Ga | $<10^{-3}$ [92] | Ti | $4 \times 10^{-3}$ [88] |
| Hg | 0.14 [92] | V | 0.06 [88] |
| In | $9 \times 10^{-3}$ [88], 2.82 [91] | Zn | $<10^{-3}$ [91] |
| Mg | 0.093 [91] | | |

phase diagram have no miscibility gap in it, and Se therefore forms mixed crystals with tellurium. With data on the $Te_nX_m$-Te phases and its position within the phase diagram, the segregation of intermetallic compounds of tellurium can be evaluated through k too, as seen in Table 8.

It can be seen that except for Se, Cd, Sb, Si, S and Hg, all the other impurities exhibit very small values of $k_{eff}$ and therefore easy to remove. Except for selenium, however, all other impurities unfavourable for zone melting, e.g. Cd and Sb, can be easily removed by vacuum distillation. The $K_{eff}$ can also be temperature-dependent [86]. Thereby, higher temperatures of molten zone may affect the diffusion coefficient D and hence the $K_{eff}$ negatively. This is especially evident for impurities such as Ag, Cu, As, Mn and Ti. An example reported in the study is the $K_{eff}$ of $2 \times 10^{-4}$ for Ag at 500°C, compared to $4 \times 10^{-2}$ at 620°C, a two orders of magnitude change.

### *3.2.2. The issue with selenium*

In addition to the problematic of effective distribution coefficient of selenium, which is close to unity, some features of selenium have the same crystal structure as tellurium and form a homogenous solid solution with that.,. Therefore, selenium removal seems to be difficult in normal conditions by zone refining. In order to overcome high levels of selenium content in tellurium (>1 ppmw), in some cases, previous treatment with hydrogen gas is carried out [72,86]. In another case, hydrogen atmosphere is maintained during the process of zone refining to separate and reduce the selenium content. Chemical reaction of hydrogen gas with selenium produces hydrogen selenide ($H_2Se$) that remains in gaseous phase at room temperature and is removed from the system by gas flow. This treatment has also the advantage of preventing oxidation of the material. Also, major selenium, oxygen and nitrogen content are drastically reduced when larger zone lengths are used. It is proved that zone size between 3 and 6 cm is the optimum for all impurities reaching 7N purity grade.

**Table 8.** Distributions coefficients (k) for intermetallic compounds $Te_nX_m$ in tellurium [96].

| Telluride | k | Telluride | k | Telluride | k |
|---|---|---|---|---|---|
| ssssCuTe | $8 \times 10^{-7}$ | $In_2Te_3$ | $6 \times 10^{-3}$ | $SnTe_2$ | $1 \times 10^{-3}$ |
| AgTe | $2 \times 10^{-6}$ | TiTe | $2 \times 10^{-4}$ | $PbTe_2$ | $1 \times 10^{-3}$ |
| $AuTe_2$ | $7 \times 10^{-5}$ | CdTe | >1 | CrTe | 0.2 |
| $As_2Te_3$ | $1 \times 10^{-3}$ | MgTe | $2 \times 10^{-4}$ | NiTe | $9 \times 10^{-4}$ |
| $Sb_2Te_3$ | $3 \times 10^{-3}$ | CaTe·Te | $8 \times 10^{-4}$ | $FeTe_2$ | $5 \times 10^{-3}$ |
| $Bi_2Te_3$ | $9 \times 10^{-5}$ | HgTe | 0.05 | $Al_2Te_3$ | $8 \times 10^{-9}$ |
| GeTe | $6 \times 10^{-4}$ | | | | |

It was confirmed that the purity of the gas affects the efficiency of purification [76]. Oxygen, water, carbon compounds and nitrogen are found in hydrogen cylinder with undesirable contents. An alternative is to produce gas by electrolysis of nan pure water and then using molecular sieve to remove oxygen andmoisture, or use high purity gas – 4N grade and above [89,97]. Some trials showed that it took 20 days in a continuous quadruple zone refining (QZR) to reduce selenium from 115ppmw to 5.6ppmw, which is an unreasonable time duration and insufficient final purity as well [67,72]. Therefore, the reduction of selenium content to ~ 1ppmw is mandatory before initiating zone refining. After zone refining, the content of selenium could be decreased to values <10 ppbw.

## 4. Summary and outlook

This article reviews the recovery and purification of tellurium from primary and secondary sources. Primary production of tellurium has been the state of the art for several decades as it is a well-established sub-line of the primary copper production. They are normally found within the anode sludge after copper refining electrolysis and are recovered through hydrometallurgical methods and subsequently electrolysis. Having a complete metallurgical process is however not the case for secondary production i.e. recycling of tellurium, as the demand for it is quite low and traditional production of tellurium tends to meet the market demand. In addition to that, tellurium end-of-life materials seems not to be as much available as other metals such as aluminium and iron. Furthermore, metallurgical processes for recovering tellurium from materials such as photovoltaics CdTe and the thermoelectric $Bi_2Te_3$ or PbTe are not mature enough to extend the laboratory scaled experiments into commercialised operations. On the purification of tellurium, vacuum distillation and zone refining are the state-of-the-art methodologies, the feasibility of which has been proven by numerous literature studies and investigations. The concept of separation coefficient and impurities are described and discussed within this article; however, the discussion included is mostly for the case of refining primary tellurium. This motivates a separate field of study for applying such purification processes on the materials from secondary route. In this case, it is worth to investigate how tellurium can be extracted from scraps to the highest yield, and how this recovered tellurium can be purified to high purity i.e. 5N and above. The development, acquirement and utilising of such processes, which includes fewer or shorter steps in comparison to the primary chain, could potentially narrow the gap for proceeding into a circular economy.

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