Innovative approach for producing high-purity tellurium (An extended abstract)

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Abstract

With the EU heavily reliant on imported tellurium, this study aims to provide a sustainable alternative by refining and remanufacturing tellurium into high-purity raw materials for reuse in similar applications, contributing to resource efficiency and supply security. This paper explores the application of advanced fractional crystallisation technique – Cooled Finger for the refinement of tellurium, offering a more time efficient alternative to the traditional zone melting method. Zone melting may take up to 200 hours to purify from 99.999% (5N) to 99.9999% (6N). Although the Cooled Finger technique is not novel, its innovative application to tellurium represents significant advancements in refining speed and overall efficiency. By utilising the varying solubility of impurities such as Cu, Ni, Fe, Bi, As, Pb and Se in the solid and liquid phases, this method enables targeted removal of impurities.

Two challenges with zone melting to date include low metal yield and long processing time. Through parameter optimization, the process has been made more efficient, particularly in reducing the reaction time. Successful trials have demonstrated the ability to refine tellurium from 99.99% (4N) to 99.997% (4N7) purity in less than 20 minutes. This quick refining has also resulted in substantial reductions in key impurities, such as As, Cu, Na, Zn, and Ni. This paper also suggests several distribution coefficient values for tellurium in the Cooled Finger method.

Introduction

Entering the 21st century, tellurium has found applications in several important sectors, such as solar cells in the form of CdTe and thermoelectric materials in the form of Bi_2Te_3 alloyed with either Sb or Se [1]. In these applications, the required purity of initial materials for fabrication is usually 5N (99.999%) or above, with the potential to increase to 6N (99.9999%) due to the growing demand for improved material properties. For these levels of purity, the state-of-the-art production uses the zone melting process, a fractional crystallisation-based method. As reported in [2], purification from 3N85

(99.985%) to 5N7 (99.9997%) was achieved on a laboratory scale using 400 g of input material after approximately 75 hours of zone melting over 5 cycles. Industrial production of high-purity tellurium follows a similar trend of requiring long processing times.

The Cooled Finger method, like zone melting, is based on the principle of fractional crystallization. This process relies on the difference in solubility of elements or impurities between the solid and molten phases of a metal [3], [4]. The process is often characterized by a distribution coefficient, k, defined as:

$$k = \frac{C_s}{C_L} \tag{1}$$

in which C_s is the concentration of element in the solid phase, and

C_L is the concentration of element in the liquid phase.

The distribution coefficient represents the theoretically achievable refining efficiency, typically in a binary system. However, the same coefficient has also been applied to intermetallic compounds, as reported in [1], [5]. For a binary system, this coefficient can be calculated from the phase diagram at a given temperature, under the assumption of complete diffusion of the solid into the liquid, i.e., the equilibrium coefficient. This coefficient can take values either less than or greater than one. Elements with $k < 1$exhibit limited solubility in the target metal, while those with $k > 1$ exhibit higher solubility. In metal refining, elements with $k > 1$ are undesirable because impurities tend to concentrate in the solid phase. It is important to note that the distribution coefficient values depend on both the equilibrium temperature and the concentration ranges (compare Fig. 1).

In addition to the distribution coefficient values, Burton, Prim, and Slichter (BPS) [6] proposed a more realistic approach by considering the diffusion layer thickness, the growth rate of the solid phase, and the diffusion coefficient of the elements. The effective distribution coefficient, k_{eff} under the BPS model is shown in the equation below:

$$k_{eff} = \frac{k}{k + (1 - k) \cdot \exp(-\frac{V\delta}{D})} \tag{2}$$

in which V is the growth rate of the solid phase,

δ is diffusion boundary layer thickness, and

D the diffusion coefficient of element.

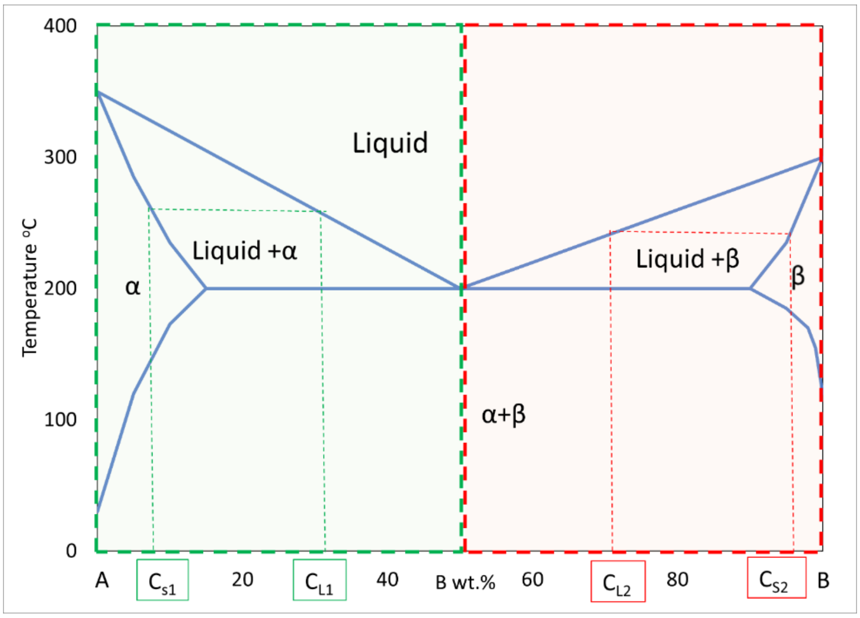

Figure 1: Eutectic binary diagram with $k < 1$ when B is < 50 wt.% (green area) and $k > 1$ when B > 50 wt. (red area)

This study explores the feasibility of refining tellurium using the Cooled Finger method, with a focus on determining the distribution coefficients (k values) for key impurities, including Al, As, Bi, Cu, Fe, Na, Ni, and Zn. Preliminary results highlight the potential of this method for impurity separation and offer initial insights into the behavior of these elements during refining. Although this work is primarily a proof of concept, the findings indicate promising opportunities for further optimization and application in tellurium purification. This abstract highlight the methodological viability and lays the groundwork for more comprehensive investigations to be presented in future publications.

2 Materials and Methods

A series of 6 experimental trials were conducted to investigate the feasibility of refining tellurium using the Cooled Finger method. The experimental setup is illustrated in Figure 2. Due to tellurium's tendency to volatilize even below its boiling point, the material and crucible were placed inside an enclosed steel chamber continuously flooded with argon gas. Around 6kg of Tellurium was melted at 470 °C under an argon atmosphere, after which a compressed air-cooled rotating shaft was immersed into the melt. The target metal crystallized on the graphite cover attached to the rotating shaft. The key controlled parameters were the rotation rate (in RPM) of the shaft and the flow rate of the compressed air (i.e., cooling gas rate in L/min).

After crystallization, samples were collected from both the crystallized solid phase (C_S) and the remaining liquid phase (C_L). The initial tellurium material had a purity of 99.99 wt.% (4N), with the specific impurities listed in Table 1. To explore the potential for a continuous Cooled Finger process, two additional experiments were conducted using the remaining liquid phase as the starting material.

A detailed list of experiments, including their parameters, is provided in Table 2. All collected samples were analyzed using ICP-OES (Spectro Acros, AMETEK Material Analysis Holdings GmbH).

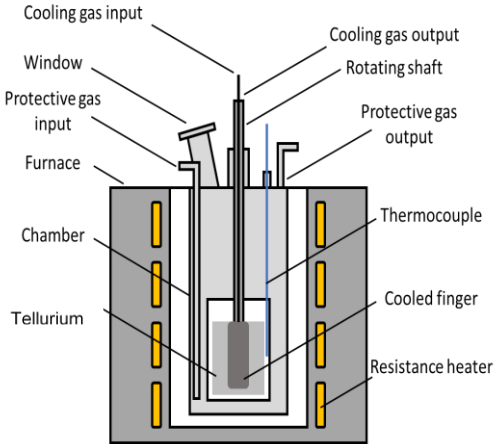

Figure 2: Experimental setup for the Cooled Finger process

Table 1: Impurities concentration in initial material given in ppmw measured by ICP-OES

Al	As	Bi	Cu	Fe	Na	Ni	Zn
0.2	< 3.75	< 3.18	11.2	20.36	33.11	4.58	10.32

Table 2 : List of experiments and parameters

Test	Rotation Rate [RPM]	Cooling gas rate [L/min-Litres per min]	Input Materials
1	80	50	4N
2	90	50	Remaining Liquid from Test 1
3	100	50	Remaining Liquid from Test 2
4	100	60	4N
5	100	70	4N
6	100	40	4N

3 Results and discussion

To evaluate the Cooled Finger process, the experimentally observed distribution coefficient (k_{exp}) for each element was calculated using Equation (1). For elements with concentrations below the detection limit, the limit value was used for calculations and is marked with an asterisk in the tabulated results (Table 3). Values reported by other researchers are also included in the table for comparison.

Among the elements analyzed, iron (Fe) exhibited the largest deviation. Most tests showed enrichment of Fe in the crystallized metal, except for the first test, which yielded results comparable to reported values. This discrepancy may be attributed to potential contamination during the sampling procedure, particularly when metallic samples were crushed into powder for ICP-OES analysis.

The k_{exp} values for other elements qualitatively align with the trends reported in the literature, i.e., $k < 1$, despite significant quantitative deviations in the absolute values For example, the calculated k value for As in this study lies averaged at roughly 0.6, while literature values reported to be within 0.0002 and 0.009. Since the distribution coefficient depends on several factors—including temperature, initial concentration, process conditions, and equipment—which varied substantially between the studies and therefore deviations between the experimental values and literature values are expected. Nevertheless, all elements except Fe exhibit the same qualitative trend (k<1) as the literature values.

Table 3 : K_{exp} calculated using chemical results from ICP-OES analysis of the refined metal and the metal melt in the crucible.

Samples	**Al**	**As**	**Bi**	**Cu**	**Fe**	**Na**	**Ni**	**Zn**
Test 1	0.58	1.00*	0.69*	0.58	0.03	0.06	1.00*	0.25
Test 2	0.97	0.62	0.69*	0.07*	1.10	0.53	0.42	0.88
Test 3	1.03	0.80	0.82	0.43	1.58	0.57	0.39	0.91
Test 4	0.50	0.12	0.86	0.32	1.17	0.82	0.82	0.55
Test 5	0.56	0.94	0.83	0.58	1.38	0.67	1.09	0.62
Test 6	0.82	0.72	0.92	0.57	1.78	0.63	0.64	0.69
Literature range[1]	0.035-0.19	0.009-0.0002	0.5	0.011-0.23	0.02-0.26	N.A	0.04-0.58	0.001
*Limit value of ICP-OES analysis used for calculations								

The overall refining efficiency of the Cooled Finger method applied to tellurium (Te) was also evaluated, and the results are presented in Figure 4. The refining efficiency was calculated using Equation (3), which accounts for the change in the total amount of impurities after crystallization.

$$\eta = \left(1 - \frac{\sum C_{s(i)}}{\sum C_{0(i)}}\right) * 100\% \tag{3}$$

$C_{s(i)}$: Concentration of element (i) in the solid phase

$C_{0(i)}$: Concentration of element (i) in the input material

(i): Al, As, Bi, Cu, Fe, Na, Ni, Zn

Test 1, conducted at 80 RPM and 50 L/min stands out as the most successful, achieving the highest refining efficiency (70.74%) and the greatest improvement in final purity, reaching 4N7. In this test, the crystal growth rate (V) was calculated to be 10.99 µm/s, derived from the radius of the crystallized metal and the crystallization time extracted from a time-temperature graph (see Figure 4). However, refining efficiency drops significantly in Test 2 (41.86%) when the rotation rate is increased to 90 RPM and turns negative in Test 3 (-0.49%) at 100 RPM. It is important to note that Tests 2 and 3 were conducted pseudo-consecutively, meaning they started with a lower initial purity compared to Test 1. The increased impurity levels may have led to localized accumulation, disrupting the diffusion process despite the higher rotation rate, which should theoretically enhance diffusion.

The negative refining efficiency, i.e., the enrichment of impurities, can likely be attributed to cross-contamination during sample preparation, as reflected in the k_{exp} values for Fe. Although no clear correlation between rotation rate and refining efficiency was observed, a higher rotation rate was selected for subsequent tests due to its potential to reduce the diffusion boundary layer thickness (δ) (as described in Equation 2) and promote more uniform heat and mass transfer within the melt.

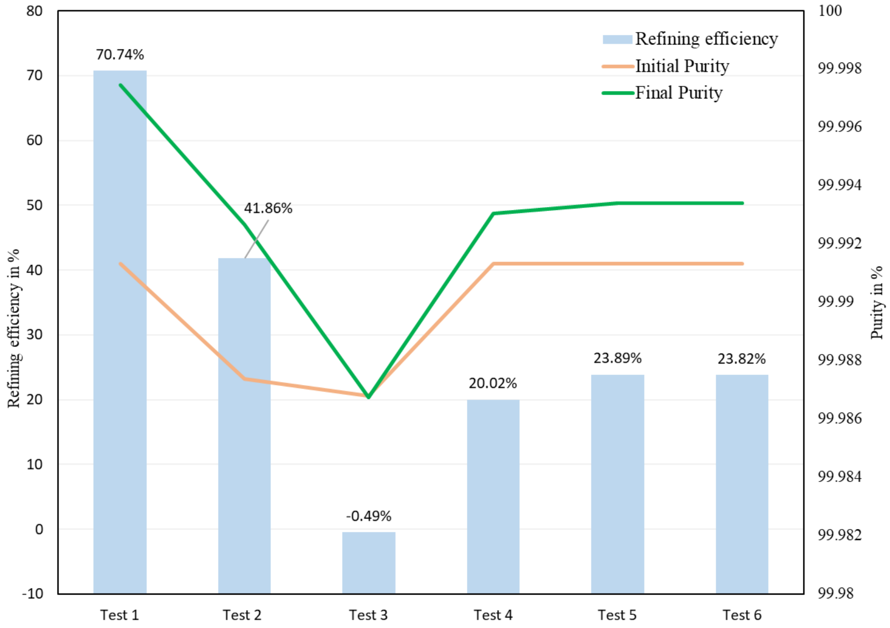

Figure 3 : Refining efficiency of Cooled Finger process

The next three tests, conducted at 100 RPM with cooling gas rates of 60, 70, and 40 L/min showed some recovery, with refining efficiencies stabilizing around 20–23%. However, they failed to match the performance of Test 1. The crystal growth rates (V) for these tests were 16.67 µm/s, 18.69 µm/s, and 10.71 µm/s, respectively. Despite variations in crystal growth rate and cooling gas rate, no significant impact on refining efficiency was observed, which contradicts the theory that slower crystal growth rates are beneficial for refining processes [7]. This discrepancy can be explained by the lack of a significant temperature gradient between the Cooled Finger and the melt bath. Unlike the Cooled Finger process used for refining aluminum [7], [8], [9], the current setup is an enclosed system where the graphite shaft remains inside the heating chamber throughout the process. As a result, the temperature of the graphite shaft remains close to that of the system, unlike in aluminum refining, where the shaft is inserted shortly before crystallization begins. This results in minimal changes in heat dissipation, even with 10 L/min intervals in cooling gas rate, leading to only minor adjustments in temperature distribution. Additionally, the differences in crystal growth rates were insufficient to alter the crystallized structure, as all tests produced equiaxed grains, as shown in Figure 5.

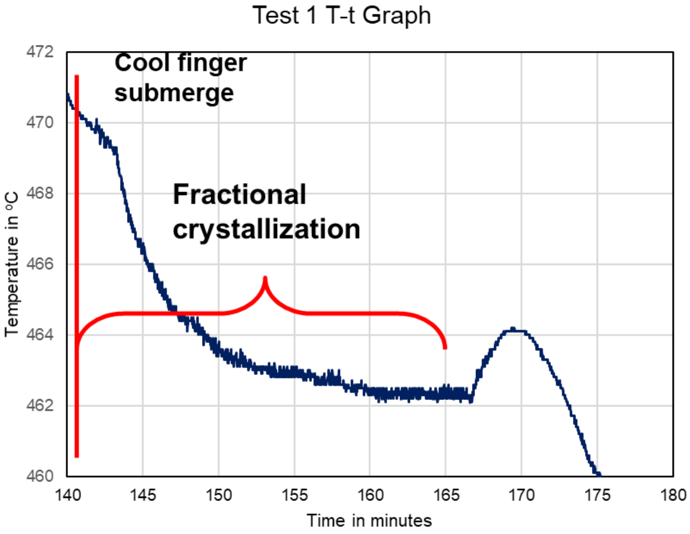

Figure 4 : Temperature -time graph of Test 1

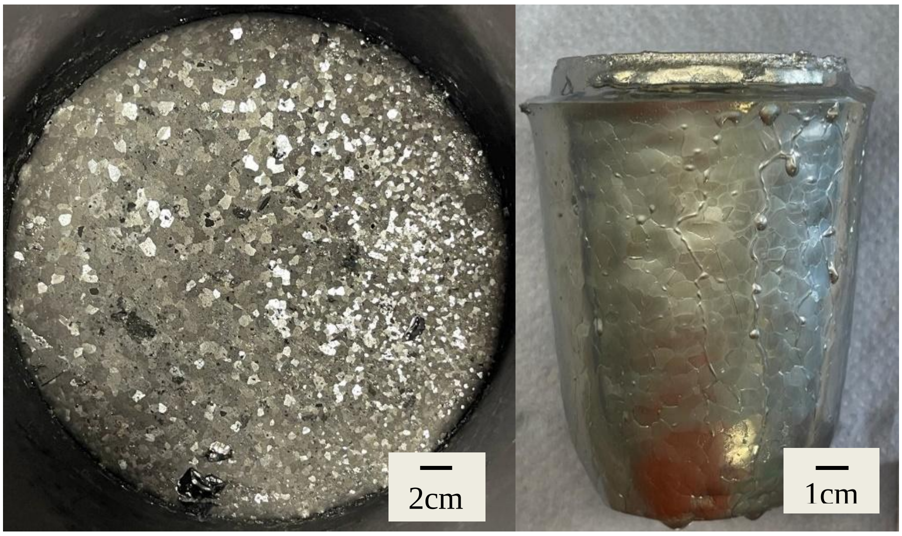

Figure 5: Equiaxed crystallised structure of crucible remaining (Left), Cooled Finger (right)

4 Summary

This extended abstract demonstrates the application of an innovative process in comparison to the state-of-the-art method, zone refining, for the refining of tellurium. The Cooled Finger process successfully refined 4N tellurium to 4N7 within a remarkably short time of 19 minutes, significantly faster than the zone melting process. The experimentally determined distribution coefficients (k_{exp}) align with reported values for most elements, except for iron (Fe), where cross-contamination during sample preparation likely contributed to elevated Fe levels in the samples. Further analysis, including evaluation of the diffusion boundary layer thickness using the BPS model, individual refining efficiencies of elements, process yield, comparison with phase diagram calculations, and parameter optimization, will be detailed in a separate scientific publication.

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