Research Article

Profound purification of tellurium, zinc and cadmium for electronic applications

Vladimir N. Abryutin[1], Elena V. Davydova[1], Mikhail A. Egorov[1], Igor I. Maronchuk[1], Daria D. Sanikovich[1]

1 ADV-Engineering, LLC, 3B 1st Lyusinovsky Lane, Moscow 119049, Russia

Corresponding author: Igor I. Maronchuk (igimar@mail.ru)

Citation: Abryutin VN, Davydova EV, Egorov MA, Maronchuk II, Sanikovich DD (2022) Profound purification of tellurium, zinc and cadmium for electronic applications. *Modern Electronic Materials* 8(1): 7–14. https://doi.org/10.3897/j.moem.8.1.89297

Abstract

A combined method of profound purification of Cd, Zn and Te developed by the Authors and allowing one to produce high-purity materials in a vertical reactor unit has been considered. The method includes the following processes: filtration refinement of metal alloy with the possibility of its vacuum degassing and additional purification through an oxide layer; first distillation with the possibility to use gettering additions in the melt and gettering filters; melt degassing with the removal of highly volatile impurities to the condenser in rough vacuum; second distillation and metal casting for weighed quantities. The Authors have developed and produced a test model of the unit for the experimental profound purification of metals using the method developed herein. Physical experiments have been conducted for obtaining 99,9999 wt.% purity Cd, Zn and Te for 30 residual impurities with a product yield of at least 55%.

Keywords

cadmium, zinc, tellurium, impurity composition, purification methods, filtration, vacuum distillation, mass spectrometry.

1. Introduction

Currently Cd, Zn and Te with a purity of not less than 99,9999 wt.% (6N) are used as components of 2-6 semiconductor compounds with permanently growing application fields. The reliability and efficiency of devices on the basis of these semiconductor compounds are determined by their purity, with the number of controlled residual impurity increasing constantly [1, 2].

The most widely used high-purity Cd, Zn and Te purification methods are rectification [3,4], distillation [5–10] and crystallization [10–12]. Despite the high efficiency of rectification methods for production of 99,9999 wt.% purity metals the use of rectification methods for these materials has remained at a level of laboratory experiments

[13] due to the complexity of equipment required for the method. A simple single or multiple distillation setup has a low yield (30 to 60%) and does not provide for high purification (within 99,99935 wt.%) [14, 15]. Higher purity materials are produced using improved distillation techniques, e.g.:

– gettering filters [16] and gettering impurity [17, 18];
– preliminary melt filtration and flashing off highly volatile impurities [16];
– use of barrier oxide layer [14];
– condenser surface heating [19].

However the currently available process solutions are usually cumbersome and expensive. Crystallization refinement methods (directional crystallization, melt growth and zone melting) are mainly used at final purification

stages for the removal of small impurity quantities from the melt. these methods allow producing metals with a purity of up to 99,99998 wt.% [10, 11] and can in most cases be combined with other refinement methods. All the above described metal refinement methods are often used in combinations within various process solutions and using different equipment, which is a negative factor because material purified with a specific method usually has to be reloaded into other equipment, i.e., additional process operations are carried out which cause surface contamination and material oxidation.

The aim of this work is to develop a combined method for the purification of Cd, Zn and Te to above 6N which would unify different refinement methods within a single process cycle and could be implemented on a single equipment unit without inter-stage material reloading. Another task is to develop test equipment and experimentally check the suitability of the technical solutions accepted.

2. Fundamentals of combined Cd, Zn and Te metal purification method

When designing a combined cadmium, zinc and tellurium refinement method and developing new-generation equipment we used many-year practical research, development and production experience in the production of high-purity materials accumulated by the workers of ADV-Engineering, LLC [20–22] which allowed us to put forward a new method and a new device [23, 24]. The main objective was to develop a reproducible method of obtaining Cd, Zn and Te with the preset purity (at least 6N) and impurity composition while keeping its cost low (in comparison with international counterparts) and hence ensuring a low price. Solving this task will provide for a competitive startup of this product in Russian and international markets. Furthermore the implementation of this method will require simple process equipment having high output and performance.

The method and device on its basis provide the possibility of running the entire process within a single cycle (one loading of the material into the reactor) without reactor opening or material reloading, including several combined metal refinement methods. The method is implemented in a device having a vertical reactor with fittings (see Fig. 1). During process operation the reactor is located in a multi-zone resistive heater the heat profile of which is changed in the course of consecutive process stages via a temperature gradient.

The device reactor consists of a quartz retort 9 and a cooled metallic flange 15 hermetically connected with the retort via air-proof seals. The flange 15 is connected to a gas-vacuum line via ports 17 which allow depressurizing the reactor to $5 \cdot 10^{-5}$ mm Hg or to an excessive inert gas (argon or nitrogen) pressure of within 0.3 kgN/cm^2.

The reactor fittings are made from electronic grade quartz or high-density graphite, at least MPG-6 Grade, depending on the physicochemical properties of the material to be purified. It is also acceptable to use combinations of graphite and quartz fittings, e.g. crucibles (1, 2, 3, 6, 8) and funnels (13) can be made from graphite whereas the rest of the fittings can be made from quartz.
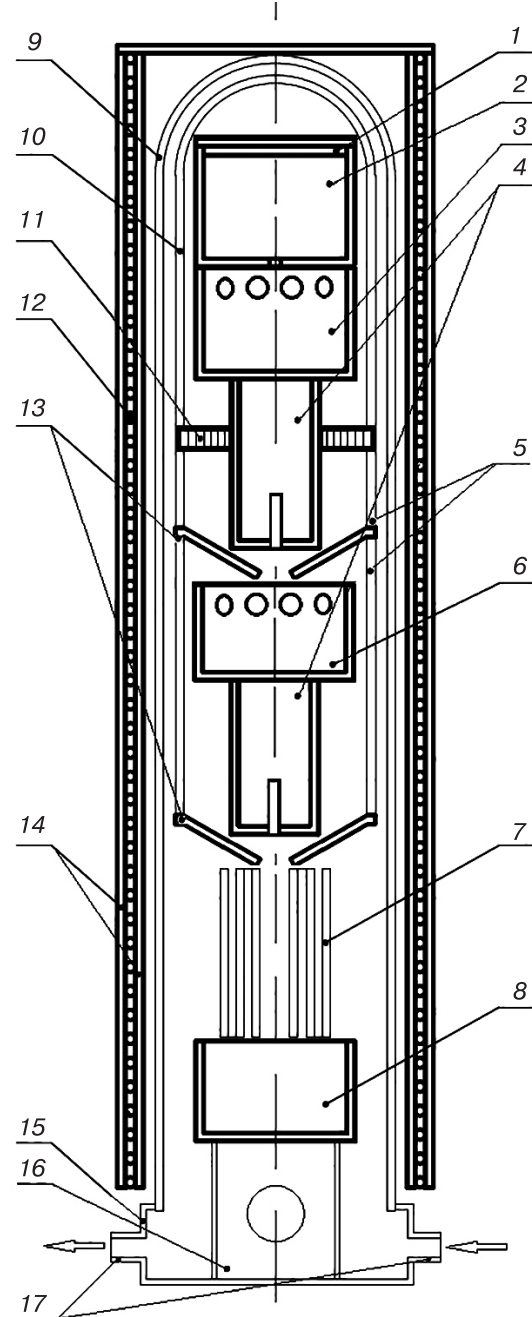
Figure 1. Schematic of metal purification unit reactor: (1) charging crucible cover, (2) charging crucible, (3) first distillation crucible, (4) distillation crucible support, (5) distillation section supports, (6) second distillation crucible, (7) condenser, (8) receiving crucible (9) quartz retort (reactor), (10) distillation section retort, (11) gettering filter, (12), heaters, (13) distillation funnel, (14) corundum muffle, (15) flange connected to the gas a vacuum lines, (16) receiving crucible support, (17) ports of gas (inlet) and vacuum (outlet) lines.

After the loading of the weighed quantity of the source metal into a charging crucible *2* the crucible is tightly closed with a cover *1* and the reactor and its fittings are assembled bottom to top by stepwise addition of each component. If necessary a weighed quantity of a gettering impurity is loaded into a first distillation crucible *3*, and a support with a gettering filter *11* is installed. After a distillation section retort *10* is installed a quartz retort (reactor) *9* is mounted and tightly connected with the flange *16* using vacuum rubber seals. The quartz retort is connected with the metallic flange via the rubber seal using a standard setup and standard process solutions. The air tightness of the assembly is controlled by depressurization of the reactor and in-leakage monitoring.

The vacuum line is prepared for the process by turning on the roughing vacuum pump, the oil-vapor (diffusion) vacuum pump and the gas line. Following the completion of these operations the reactor is placed into the heater which contains the muffle *14* and the heaters *12* and heating is switched on for gradual achievement of the temperature profile in the unit as is required for the starting stage of the process, i.e., the filtration of the source material from the charging crucible *2* to the first distillation crucible *3*.

The crucibles are tightly installed one onto the other through a grooved coupling. The charging crucible has the tightly closed cover *1* and features a slight taper of the inner part which provides for comfortable unloading of the crucible remainder, and its bottom part has a required number of filtering holes 0.7–1.0 mm in diameter (depending on the properties, purity and oxidation degrees of the source material), The crucible is made from a material non-wettable by the source metal melt but wettable by its oxides. Filtration occurs at up to $1 \cdot 10^{-3}$ mm Hg and charging crucible and first distillation crucible temperatures that are 80–120 K above the metal melting point (depending on source material properties). The temperature below the crucible, down to the condenser *7*, should be maintained equal or slightly above (by not more than 10 K) the purified metal melting point. The condenser temperature should be below the metal melting point (by at least 10 K). The principle of the filtration process is that the melting of the source metal is followed by the refinement of the melt due to its passage through the filtering holes. This causes mechanical separation of large nonmetallic inclusions and adhesion cleaning of fine nonmetallic inclusions which remain in the melt. Furthermore the filtered metal is supplied to the bottom crucible by batches thus favoring intense removal from the well-developed surface of the pouring metal of gas bubbles and inclusions as well as highly volatile impurities which condense on the condenser because to the process is arranged as described above. The melt surface in the charging crucible is covered with an oxide film formed by natural oxidation of pieces of the source metallic charge placed into the crucible for melting. This oxide film traps a number of heavy impurities. The oxide film wets the crucible surface and its surface tension prevents the entire melt from

filtering into the first distillation crucible. The filleting holes and their number are selected so that, depending on the properties of the material being purified, its contamination and oxidation degrees, the filtration process can be stopped due to surface tension and wetting when the quantity of the crucible remainder is ~15% of the source material charge. However filtration does not stop at this stage, and further purification, more profound and complex, continues throughout the rest of the process. This is primarily due to the crucible cover which maintains the residual pressure in the crucible higher than the residual pressure in the reactor. Passing through the oxide layer and thus undergoing refinement the metal vapors increase the residual pressure in this volume thus pressing on the melt and violating the equilibrium with the melt surface tension. Thus filtration carries on slowly, the crucible pressure reaching a specific level and not growing any further because the vapors leave the crucible from under the crucible cover to the distillation section of the reactor and condense along with the rest of the purified metal. At the end of the entire process the quantity of crucible remainder is at least ~10% of the overall source metal charge.

The second stage of the process is the first distillation of the filtered material. The filtered metal is in the first distillation crucible *3* made from a material that is not wetted by the melt of the metal being refined. The inner part of the crucible features a slight taper for comfortable unloading of the crucible remainder. The volume and size of the crucible *3* are comparable with those of the charging crucible. The overall area of the process holes in the top part of the crucible *3* should be at least 20% of the melt area in the crucible for controlling the rate of mass transport during distillation. This stage of the process may develop following various structural scenarios. Under the first scenario the crucible *3* is charged with a weighed quantity of a gettering material which chemically binds one or more impurities in the metal being refined to form compounds which stay in the crucible remainder during further distillation [17]. Under the second scenario the getter is not added. Here everything depends on the properties and contamination of the source material.

The crucible *3* is mounted onto the support *4* having process slots/holes in the bottom part which rests on the distillation draining funnel *13*. The funnel *13* is fixed on the second distillation crucible *6* located underneath. During assembly the spaces relating to different process stages are isolated from one another with the retort *10* and the supports *5* of the distillation section. The gettering filter *11* is fixed between the retort *10* and the top support *5* and, by analogy with the gettering impurity, is used in the process as required thus allowing the process setup to be extended by two more structural units. The function of the filter is to absorb gaseous impurities released during distillation and to reduce their content in the condensate. Furthermore the elevated activity of the getter to oxygen provides for the condensation of volatile metal oxides on the getter which provides for further purification from

metallic impurities. The filter is in the temperature zone corresponding to the refined metal evaporation point and therefore it traps particles of the main material [15].

The second process stage is carried out at a reactor residual pressure of $(0,5–5,0) \cdot 10^{-4}$ mm Hg. The temperature profile in the reactor has the following diagram:

– the temperature at the crucibles *2* and *3* is 50–60 K above the refined metal melting point;

– the support *4* has a negative temperature gradient ending at the top funnel *13* where the temperature is equal to the refined metal melting point;

– the temperature at the section before the second funnel is maintained 20–30 K below the refined metal melting point;

– the temperature at the condenser *7* is lowered to the minimum possible level (depending on the equipment design).

The distillation process is as follows. The metal evaporating from the melt surface passes through process holes in the crucible, then through the gettering filter and finally condensates on the funnel. The elements and compounds having a higher vapor pressure than that of the main refined metal are highly volatile impurities, while the elements and compounds having a lower vapor pressure are low volatile impurities and concentrate in the crucible remainder. The rate of distillation (mass transport) is determined by the temperature level, residual pressure in the reactor and the ratio between the area of the process holes and the evaporation surface area; this ratio is found experimentally depending on the process modes used and the properties of the material being refined. Some of the highly volatile impurities condense on the gettering filter and others, on the condenser in the course of distillation. When the quantity of the crucible remainder is 20% of that of the filtered material, distillation refinement should be stopped by filling the reactor with an inert gas until its residual pressure is equal to the atmospheric one. Then the temperature at the top funnel *13* and at the second distillation crucible *6* should be increased to 90 K above the refined metal melting point while draining the distillate to the crucible *6*. It should be noted that at further process cycles distillation from the crucible *3* will continue slowly and finally the level of the crucible remainder will decrease to ~17% of the filtered material weight.

At the next third stage, degassing of highly volatile impurities at low vacuum is conducted. This operation includes two phases during which the temperature of the melt in the second distillation crucible *6* is cycled over a wide range. Both phases are conducted at low vacuum with a residual pressure of up to $1 \cdot 10^{-3}$ mm Hg in the sub-reactor space. At the former phase the temperature levels in different zones of the unit are maintained as follows:

– the temperature at the crucibles *2* and *3* and up to the top funnel inclusively is maintained (if possible) at 20–30 K above the refined metal melting point;

– the temperature at the second distillation crucible *6* is maintained at 80–120 K above the metal melting point;

– up to the second funnel there is a temperature gradient ending at 20–30 K above the melting point;

– the temperature at the condenser *7* is maintained at the lowest possible level.

After the equipment reaches this operation mode the unit is held under these conditions for 20 to 30 min.

At the second phase of the third stage the temperature at the second distillation crucible *6* is lowered to 20–30 K above the melting point at the maximum possible rate, the other process modes being unchanged. After holding for 20 to 30 min the temperature is brought to the level corresponding to the first phase. The operation is repeated several times depending on the properties and contamination level of the metal being refined.

This two-phase cycle ensures the separation of gas bubbles and inclusions from the surface and the removal of volatile impurities during melt agitation due to a variation of the melt temperature gradient. The impurities and inclusions considered above as well as a small part of the refined metal condense on the condenser.

The next fourth stage includes the second distillation of the refined metal. The melt is in the second distillation crucible *6* which is made from a material non-wettable by the refined metal melt and features a slight taper inside for comfortable unloading of the crucible remainder. The volume and size of the crucible *6* are 15% smaller than those of the first distillation crucible *3*, the process holes in the top part of this crucible being identical to those in the first distillation crucible.

The crucible is mounted on the bottom support *4* having process slots/holes in its bottom part, the bottom support being in turn installed on the bottom distillation draining funnel *11* fixed on the condenser *7* located underneath. The process volumes relating to different process stages are separated by the bottom support *5* of the distillation section.

The fourth stage by analogy with the second one is carried out at a reactor residual pressure of $(0,5–5,0) \cdot 10^{-4}$ mm Hg. The temperature profile in the reactor is set up as follows:

– the temperature at the crucibles *2* and *3* and up to the top funnel inclusively is maintained at 10–15 K above the refined metal melting point;

– the temperature at the second distillation crucible *6* is maintained at 30–40 K above the metal melting point;

– the support *4* has a negative temperature gradient ending at the bottom funnel *13* where the temperature is equal to the refined metal melting point;

– the temperature at the condenser *7* is lowered to the minimum possible level.

Distillation is conducted as follows. The metal evaporating from the melt surface passes through process holes in the crucible and condenses on the funnel, by analogy with the second stage, except that the temperature at the melt surface is lower and hence the distillation rate is smaller and the refinement process is more efficient. When the crucible remainder is 15% of the quantity of the filtered material, the process is stopped by filling

the reactor with an inert gas until its residual pressure is equal to the atmospheric one. Then the temperature at the bottom funnel *13* is increased to 90 K above the refined metal melting point and the temperature in the receiving crucible *8* is brought to 10 K below the melting point while draining the distillate to the crucible *8*. The crucible may have various designs allowing one to produce either a single ingot or multiple ingots of the required size and shape to suit customer's needs. Furthermore the size of the as-cast ingots may depend on the diameter of the boat so to provide for its more compact loading during further crystallographic purification of the metal.

After the completion of the above operations the furnace unit is shifted away from the reactor with fittings which is cooled and then disassembled. The crucible remainders and the product material are removed, the product material being sampled and packed. The fittings and the reactor are serviced and prepared for next refining process.

3. Experimental

Design documentation was developed and a test unit with high-vacuum and gas systems was produced featuring a vertical reactor arrangement (and hence a vertical furnace unit with a six-zone heater). Test purification of Cd, Zn and Te has been conducted.

The raw materials used for purification were as follows:
– Cd0 Grade Cd as per GOST 1467-93;
– Zn0 Grade Zn as per GOST 3640-94;
– Te-improved Grade Te as per TU 20.13.21-096-00194429-2020.

Before loading into the unit a test sample was taken for studying the elemental composition of the raw materials. Cd was placed into the charging crucible beforehand in the form of an as-cast ingot, and Zn and Te were placed by pieces separated from the source ingots. The purification of different materials was conducted in individual reactors and fitting sets for each material. The fittings used allowed loading raw Cd, Zn and Te in quantities of 2500, 2100 and 1800 g, respectively.

Combined fittings were used for metal purification: some of them were made from at least MPG-7 grade graphite as per TU1915-051-002008510 2005 and other from silica glass pipes as per GOST 15177-70. The charging crucible cover *1*, the charging crucible *2*, the first distillation crucible *3*, the second distillation crucible *6*,

the receiving crucible *8* and the distillation funnel *13* were made from graphite. The distillation crucible support *4*, the distillation section supports *5*, the condenser *7* and the distillation section retort *10* were made from silica glass. The processes were conducted strictly pursuant to the method described above but without a gettering filter and gettering impurities.

4. Results and discussion

After purification and reactor opening the crucible remainders were unloaded from the charging crucible *2*, the first distillation crucible *3* and the second distillation crucible *6*, and final product ingots were unloaded from the receiving crucible *8*. The condenser *7* was weighed before and after the experiment in order to determine the weight of the condensed material which is considered as process losses (along with the material condensed on different parts of the fittings and the flange). Data on the material balance of Cd, Zn and Te purification are summarized in Table 1. The results suggest that the profound purification method developed is efficient.

Process samples were taken at input control and from final product. The samples were prepared and forwarded for element composition study by atomic adsorption and mass spectrometry. At the Giredmet Test Center the samples were studied using atomic emission spectroscopy on a Grand high-resolution multichannel spectrometer (VMK-Optoelektronika, spectral resolution 0.012 nm) and spark mass spectroscopy on a JEOL JMS-01-BM2 double focus mass-spectrometer. Some tests were conducted at ARMOLED JSC on a NexION inductively coupled plasma mass-spectrometer. The results are summarized in Table 2. For the example of Te, impurity distributions in the material by refinement process stages are illustrated, and the data for Ca and Zn are presented for raw material and final product. Remaining tellurium after filtration was studied by atomic emission, raw and as-filtered Te and Te after first distillation was studied by inductively coupled plasma mass spectroscopy, and other samples were studied on a spark mass spectrometer. The overall impurity content in the main material in all cases (at all process stages) was calculated taking into account sensitivity limits of the test equipment for specific impurities. Table 2 shows the impurity composition determined to be functional (according to literary data [1, 2, 25, 26]) for the growth of CdZnTe and CdTe single crystals for detector element fabrication.

Table 1. Material balance of Cd, Zn and Te purification

| # | Material | Raw charge (g) | Residue (g/%) | | | Final product (receiving crucible) (g/%) | Technical loss (g/%) |
			Charging crucible	First distillation crucible	Second distillation crucible		
1	Cd	2500	262.5/10,5	410.0/16.4	395.0/15.8	1417.5/56.7	15.0/0.6
2	Zn	2100	235.2/11,2	380.1/18.1	306.6/14.6	1169.7/55.7	8.4/0.4
3	Te	1800	181.8/10,1	340.2/18.9	271.8/15.1	995.4/55.3	10.8/0.6

Table 2. Elemental composition of Te, Cd and Zn samples taken at first and final process stages from test unit

#	Impurity	Impurity content (wt.%)							
		Te				Cd		Zn	
		T-U Grade Te	Filtration residue	Filtration + 1st distillation	Purified Te	Kd–0 Grade Cd	Purified Cd	Ts–0 Grade Zn	Purified Zn
1	Ag	$2.57 \cdot 10^{-4}$	$2 \cdot 10^{-5}$	$9.92 \cdot 10^{-7}$	$<1 \cdot 10^{-6}$	$1 \cdot 10^{-4}$	$8 \cdot 10^{-6}$	$1 \cdot 10^{-4}$	$<3 \cdot 10^{-7}$
2	Sn	$<3.94 \cdot 10^{-6}$	$1 \cdot 10^{-3}$	$2.14 \cdot 10^{-5}$	$<3 \cdot 10^{-6}$	$1 \cdot 10^{-6}$	$<8 \cdot 10^{-7}$	$1 \cdot 10^{-3}$	$<4 \cdot 10^{-6}$
3	Al	$9.3 \cdot 10^{-4}$	$4 \cdot 10^{-2}$	$<2.69 \cdot 10^{-5}$	$6 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$8 \cdot 10^{-6}$	$5 \cdot 10^{-3}$	$8 \cdot 10^{-6}$
4	Ti	$2.05 \cdot 10^{-6}$	$4 \cdot 10^{-2}$	$9.68 \cdot 10^{-6}$	$<3 \cdot 10^{-7}$	$<2 \cdot 10^{-5}$	$<2 \cdot 10^{-6}$	$<2 \cdot 10^{-5}$	$5 \cdot 10^{-7}$
5	P	–	–	–	$<1 \cdot 10^{-6}$	–	$<1 \cdot 10^{-7}$	–	$<1 \cdot 10^{-7}$
6	B	$<3.55 \cdot 10^{-6}$	–	$<5.14 \cdot 10^{-7}$	$<3 \cdot 10^{-6}$	$<1 \cdot 10^{-6}$	$<3 \cdot 10^{-7}$	$<1 \cdot 10^{-6}$	$<3 \cdot 10^{-7}$
7	I	–	–	–	$<8 \cdot 10^{-7}$	–	$<7 \cdot 10^{-7}$	–	$<7 \cdot 10^{-7}$
8	Ca	$3.78 \cdot 10^{-4}$	$6 \cdot 10^{-3}$	$6.26 \cdot 10^{-4}$	$<1 \cdot 10^{-6}$	$6 \cdot 10^{-5}$	$<7 \cdot 10^{-6}$	$6 \cdot 10^{-5}$	$<7 \cdot 10^{-6}$
9	Cu	$3.1 \cdot 10^{-3}$	$4 \cdot 10^{-5}$	$1.09 \cdot 10^{-4}$	$<1 \cdot 10^{-5}$	$1 \cdot 10^{-2}$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-3}$	$9 \cdot 10^{-6}$
10	Cr	$6.31 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$1.58 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	$<2 \cdot 10^{-5}$	$<4 \cdot 10^{-7}$	$<2 \cdot 10^{-5}$	$<6 \cdot 10^{-7}$
11	Fe	$1.81 \cdot 10^{-4}$	$5 \cdot 10^{-2}$	$2.3 \cdot 10^{-4}$	$5 \cdot 10^{-6}$	$2 \cdot 10^{-3}$	$4 \cdot 10^{-6}$	$5 \cdot 10^{-3}$	$7 \cdot 10^{-6}$
12	In	$3.37 \cdot 10^{-5}$	–	$<4.87 \cdot 10^{-8}$	$1 \cdot 10^{-6}$	$<1 \cdot 10^{-6}$	$<3 \cdot 10^{-7}$	$<1 \cdot 10^{-6}$	$<3 \cdot 10^{-7}$
13	Mg	$<3.51 \cdot 10^{-6}$	$5 \cdot 10^{-3}$	$<5.08 \cdot 10^{-6}$	$<3 \cdot 10^{-7}$	$<2 \cdot 10^{-5}$	$<6 \cdot 10^{-6}$	$<2 \cdot 10^{-5}$	$<1 \cdot 10^{-6}$
14	Mn	$6.31 \cdot 10^{-6}$	$8 \cdot 10^{-3}$	$<1.06 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$4 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$<1 \cdot 10^{-6}$
15	Mo	$<4.98 \cdot 10^{-5}$	–	$<7.21 \cdot 10^{-5}$	$<2 \cdot 10^{-6}$	$<2 \cdot 10^{-6}$	$<1 \cdot 10^{-6}$	$<2 \cdot 10^{-6}$	$<1 \cdot 10^{-6}$
16	Ni	$<4.93 \cdot 10^{-6}$	$3 \cdot 10^{-3}$	$3.94 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	$4 \cdot 10^{-4}$	$<1 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$<1 \cdot 10^{-6}$
17	Pb	$1.66 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	$303 \cdot 10^{-5}$	$<6 \cdot 10^{-6}$	$2 \cdot 10^{-2}$	$2 \cdot 10^{-6}$	$1 \cdot 10^{-2}$	$1 \cdot 10^{-6}$
18	Tl	$3.99 \cdot 10^{-4}$	$<3 \cdot 10^{-7}$	$8.99 \cdot 10^{-9}$	$<6 \cdot 10^{-6}$	$3 \cdot 10^{-3}$	$2 \cdot 10^{-6}$	$2 \cdot 10^{-6}$	$<1 \cdot 10^{-6}$
19	Cl	–	–	–	$2 \cdot 10^{-6}$	–	$<2 \cdot 10^{-7}$	–	$<2 \cdot 10^{-7}$
20	Co	$9.68 \cdot 10^{-6}$	–	$2.07 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$<3 \cdot 10^{-7}$	$<2 \cdot 10^{-6}$	$<3 \cdot 10^{-7}$
21	Sb	$4.63 \cdot 10^{-6}$	–	$3.54 \cdot 10^{-6}$	$<1 \cdot 10^{-5}$	$9 \cdot 10^{-5}$	$<3 \cdot 10^{-7}$	$2 \cdot 10^{-5}$	$4 \cdot 10^{-6}$
22	Na	$3.8 \cdot 10^{-3}$	–	$5.69 \cdot 10^{-5}$	$<1 \cdot 10^{-6}$	$<2 \cdot 10^{-5}$	$8 \cdot 10^{-6}$	$<2 \cdot 10^{-5}$	$8 \cdot 10^{-6}$
23	Si	$1.8 \cdot 10^{-3}$	$<2 \cdot 10^{-2}$	$<4.43 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$9 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$<9 \cdot 10^{-6}$
24	K	$2.78 \cdot 10^{-5}$	–	$3.26 \cdot 10^{-5}$	$<1 \cdot 10^{-6}$	$<2 \cdot 10^{-5}$	$<6 \cdot 10^{-6}$	$<2 \cdot 10^{-5}$	$<6 \cdot 10^{-6}$
25	V	$9.64 \cdot 10^{-7}$	–	$6.59 \cdot 10^{-6}$	$<3 \cdot 10^{-7}$	$8 \cdot 10^{-6}$	$<4 \cdot 10^{-6}$	$<2 \cdot 10^{-6}$	$<2 \cdot 10^{-7}$
26	Li	$<1.02 \cdot 10^{-6}$	–	$5.53 \cdot 10^{-5}$	$<1 \cdot 10^{-6}$	$<1 \cdot 10^{-6}$	$8 \cdot 10^{-7}$	$<1 \cdot 10^{-6}$	$<1 \cdot 10^{-7}$
27	Cd	$3.91 \cdot 10^{-3}$	–	$<2.0 \cdot 10^{-7}$	$<2 \cdot 10^{-7}$	–	–	$4 \cdot 10^{-3}$	$2 \cdot 10^{-6}$
28	Zn	$<4.67 \cdot 10^{-5}$	–	$<7.76 \cdot 10^{-5}$	$6 \cdot 10^{-6}$	$4 \cdot 10^{-3}$	$6 \cdot 10^{-6}$	–	–
29	As	$<3.13 \cdot 10^{-6}$	–	$<4.53 \cdot 10^{-7}$	$2 \cdot 10^{-6}$	$8 \cdot 10^{-6}$	$<5 \cdot 10^{-6}$	$5 \cdot 10^{-4}$	$<4 \cdot 10^{-6}$
30	Se	$9.05 \cdot 10^{-5}$	–	$<7.31 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	$<1 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$<1 \cdot 10^{-6}$
31	S	–	–	–	$<1 \cdot 10^{-6}$	–	$<1 \cdot 10^{-7}$	–	$<1 \cdot 10^{-7}$
Total (for main material)		99.98	99.82	99.998	99.99985	99.96	99.99991	99.973	99.99992

5. Conclusions

Optimum multistage combination of different refinement processes was designed based on analysis of profound Cd, Zn and Te purification methods. A method and a device for metal purification were developed, featuring non-standard technical solutions and allowing high-purity materials to be produced using a combination of vertical reactor techniques.

The method suggested includes the following processes:

– filtration refinement of metal with the possibility of vacuum degassing and additional purification via oxide layer;

– first distillation with the possibility to use gettering additions in melt and gettering filters;

– melt degassing with the removal of highly volatile impurities to condenser at low vacuum;

– second distillation and metal casting for required weighed quantities.

A profound Cd, Zn and Te purification test unit was developed and produced. The material obtained had a purity of more than 99,9999 wt.% for 30 major residual impurities and a product yield of at least 55% of raw charge. Physical experiments confirmed the suitability of the chosen technical solutions for the development of the method and device for profound Cd, Zn and Te purification.

Acknowledgment

References

1. Kondrik A.I., Kovtun G.P. Investigation of the properties of semiconductor materials for detectors of ionizing radiation. *Tekhnologiya i Konstruirovanie v Elektronnoi Apparature = Technology and Design in Electronic Equipment.* 2003; (6): 3–6. (In Russ.). http://dspace.nbuv.gov.ua/bitstream/handle/123456789/70708/01-Condrik.pdf

2. Kondrik A.I., Kovtun G.P. Influence of impurities and structural defects on the electrophysical and detector properties of CT and CZT. *Tekhnologiya i Konstruirovanie v Elektronnoi Apparature = Technology and Design in Electronic Equipment.* 2019; (5-6): 43–50. (In Russ.). https://doi.org/10.15222/TKEA2019.5-6.43

3. Chernyaev B.N., Zernov V.B., Povedskaya L.G., Ershova S.A., Klofach I.I. Study of deep purification of cadmium and zinc by rectification and zone recrystallization. *Russian Journal of Applied Chemistry.* 1966; 39(6): 1259–1266. (In Russ.)

4. Kozin L.F., Berezhnoy E.O., Kozin K.L. Regularities of deep purification of cadmium by rectification. *Inorganic Materials.* 1999; 35(8): 940–945. (In Russ.)

5. Alexandrov B.N., Zudov V.G. Behavior of impurities in cadmium during vacuum distillation. *Izvestiya AN SSSR. Metally = Proceedings of the Academy of Sciences of the USSR. Metals.* 1974; (1): 43–47. (In Russ.)

6. Kalashnik O.N., Niselson L.A. Purification of simple substances by distillation with hydrothermal oxidation of impurities. *Vysokochistye Veshchestva = High Purity Substances.* 1987; (2): 74–78. (In Russ.)

7. Aleksandrov B.N. Obtaining and studying the properties of pure metals. In 2 vol. Khar'kov: Izdatel'stvo KhFTI; 1970. Vol. 1. P. 26–34. (In Russ.)

8. Kovalevsky S.V., Shelpakova I.R. High-purity zinc, cadmium, tellurium, indium and gallium: preparation and analysis. *Chemistry for Sustainable Development.* 2000; 8(1-2): 85–87. https://www.sibran.ru/upload/iblock/963/high_purity_zinc_cadmium_tellurium_indium_and_gallium_preparation_and_analysis.PDF

9. All S.T., Rao J.V., Varma K.S. Prakash T.L. Purification of cadmium up to 5N+ by vacuum distillation. *Bulletin of Materials Science.* 2002; 25(6): 479–481.

10. Potolokov N.A., Fedorov V.A. Ultrapurification of tellurium and cadmium by distillation and crystallization. *Inorganic Materials.* 2012; 48(11): 1212–1217. (In Russ.)

11. Pfann W.G. Zone melting. New York, Wiley; London, Chapman and Hall; 1960. 366 p. (Russ. Transl.: Pfann W.G. Zonnaya plavka. Moscow: Metallurgizdat; 1960. 366 p.)

12. Aleksandrov B.N., Verkin B.I. Purification of electrolytically pure cadmium by zone recrystallization and vacuum distillation. *Physics of Metals and Metallography.* 1960; 9(3): 362–365. (In Russ.)

13. Gorban E.P., Vivdyuk V.G., Elizarov A.I. et al. Evaluation of the purity of cadmium by the method of relative residual resistance. In: *Scientific Works of GIREDMET. Alloys of Rare Metals.* Moscow: Metallurgiya; 1980. Vol. 96: 109–113. (In Russ.)

14. Kozin L.F., Berezhnoy E.O., Kozin K.L. Patterns of deep purification of cadmium by distillation. *Vysokochistye Veshchestva = High Purity Substances.* 1996; (5): 11–29. (In Russ.)

15. Churbanova M.F., Karpova Yu.A., Zlomanova P.V., Fedorov V.A., eds. High-purity substances. Moscow: Nauchnyi mir; 2018. 994 p. (In Russ.)

16. Shcherban A.P., Kovtun G.P., Gorbenko Y.V., Solopikhin D.A., Virich V.D., Pirozhenko L.A. Production of high purity granular metals: cadmium, zinc, lead. *Tekhnologiya i Konstruirovanie v Elektronnoi Apparature = Technology and Design in Electronic Equipment.* 2017; (1-2): 55–60. (In Russ.). https://doi.org/10.15222/TKEA2017.1-2.55

17. Patent (RU) No. 2687403, Class. C01B 19/02 C22B 9/04. Grishechkin M.B., Khomyakov A.V., Mozhevitova E.N., Avetisov I.Kh. Method for producing high-purity tellure by distillation with low content of selenium. Appl.: 08.10.2018; publ.: 13.05.2019. (In Russ.). https://yandex.ru/patents/doc/RU2687403C1_20190513

18. Grishechkin M.B. Application of gas-phase technologies for deep purification of substances based on rare elements: Dis. Cand. Sci. (Chem.). Moscow; 2021. 256 p. (In Russ.)

19. Alexandrov B.N., Dyakov I.G. Purification of technical cadmium by vacuum distillation using a heated condenser. *Physics of Metals and Metallography.* 1962; 14(4): 569–573. (In Russ.)

20. Maronchuk I.I., Maronchuk I.E., Sanikovich D.D., Shirokov I.B. Development of clearing technique of metallurgical silicon to solar grade silicon. *Izvestiya Vysshikh Uchebnykh Zavedenii. Materialy Elektronnoi Tekhniki = Materials of Electronics Engineering.* 2015; 18(3): 189–194. (In Russ.). https://doi.org/10.17073/1609-3577-2015-3-189-194

21. Patent (UA) No 97576, Кл. C 01B 33/037. Maronchuk I.I., Kuliutkina T.F., Maronchuk I.E., Naidenkova M.V. Process for the treatment of silicon of technical purity. Appl.: 09.08.2010; publ.: 27.02.12. (In Ukr.). https://uapatents.com/5-97576-sposib-ochish-hennya-kremniyu-tekhnichno-chistoti.html

22. Maronchuk I.I., Maronchuk I.E., Sanikovich D.D., Gochua K.V. Purification of metallurgical silicon up to "solar" mark siliconi. *International Journal of Renewable Energy Research.* 2016; 6(4): 1227–1231. https://doi.org/10.20508/ijrer.v6i4.4355.g6910

23. Patent application (RU) No 2021117792, Cl. C01B 19/02 C22B 9/04. Maronchuk I.I., Davydova E.V., Egorov M.A., Sanikovich D.D. The method of deep cleaning of metals. Appl.: 17.06.2021. (In Russ.)

24. Patent application (RU) No 2021117786, Cl. C01B 19/02 C22B 9/04. Maronchuk I.I., Davydova E.V., Egorov M.A., Sanikovich D.D. Device for deep cleaning of metals. Appl.: 17.06.2021. (In Russ.)

25. Zázvorka J., Hlídek P., Franc J., Pekárek J., Grill R. Photoluminescence study of surface treatment effects on detector-grade Cd-Te:In. *Semiconductor Science and Technology.* 2016; 31(2): 025014. https://doi.org/10.1088/0268-1242/31/2/025014

26. Zázvorka J. Photoconductivity, photoluminescence and charge collection in semiinsulating CdTe and CdZnTe: doctoral thesis. Prague, CZ: Institute of Physics of Charles University; 2016. 49 p. https://dspace.cuni.cz/handle/20.500.11956/82430