Purification of cadmium and lead for low-background scintillators

G.P. Kovtun[a*], A.P. Shcherban'[a], D.A. Solopikhin[a], V.D. Virich[a], V.G. Glebovsky[b]

[a] *National Science Center "Kharkov Institute of Physics and Technology" (NSC KIPT), 1, Academicheskaya str., Kharkov 61108, Ukraine*
[b] *Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Russia*

The method for deep purification of Cd, ^{106}Cd and Pb, consisting in the filtration-distillation combination is offered. It is shown that these procedures are very efficient for deep purification of natural Cd and enriched ^{106}Cd, and archeological Pb (Black Sea, near Crimea, dated to I century B.C.). A reached level of the content of the most harmful elements, such as Ni, Cu, Fe, Mg, Mn, Cr, V, Co, Th, U, Ra, K, Rb, In, La, Lu, Sm is < 1 ppm. The pilot batches of high-purity Cd, ^{106}Cd and Pb, applicable for production of scintillation monocrystals (Cd,^{106}Cd,Pb)WO_4 and (Cd,^{106}Cd,Pb)MoO_4 are obtained.

1. Introduction

To produce high-quality scintillators (Cd,^{106}Cd,Pb)WO_4 and (Cd,^{106}Cd,Pb)MoO_4, the level of initial component contamination should not exceed several ppm. The most harmful elements are the following: Ni, Cd, Fe, Mg, Mn, Cr, V, Cd and radioactive elements. An increased content of Ni, Cu > 0.2 ppm and Fe, Mg, Mn, Cr, V, Co > 2 ppm leads to the coloring of crystals and to the deterioration of their scintillation properties. The concentration of radioactive elements, e.g. Th, U, Ra, K, Rb, In, La, Lu, Sm should be << 1 ppm, as their presence in crystals increases the background of a detector. Analysis of the contamination level in the available natural Cd, enriched ^{106}Cd and archeological lead has shown that the impurity content in them exceeds by tens and hundreds times the requirements to the initial materials for growing single-crystals of tungstates and molybdates of cadmium and lead.

The purification procedure should provide both the minimal losses of initial materials and the total waste conservation in the process of refining, in particular for ^{106}Cd, taking into account a high cost of this material. One of the methods of deep purification of these metals is a vacuum distillation [1-3]. The interest in distillation is due to the fact that this method enables reaching a high degree of purification with a high yield of an ecologically pure product. The goal of investigations is to develop the methods and devices for purification and production of a pilot batch of high-purity Cd, ^{106}Cd and Pb, as applied to the problems of designing of low-background scintillation detectors with the use of tungstates and molybdates of cadmium and lead. The paper presents the results of experimental investigations on the behavior of impurity elements in the natural Cd, enriched ^{106}Cd and archeological lead.

To account for the above-mentioned requirements to the final product purity and to provide minimal losses of initial materials, the procedure developed for deep purification of Cd and ^{106}Cd was based on our own earlier investigations on the cadmium purification by vacuum distillation [2-4]. In this connection, for the given case we have chosen an approach consisting in the combination of prefiltration and 2…5 distillations. Experimental investigations on the optimization of temperature and time regimes were carried out with archeological lead. For this purpose special devices for lead filtration and distillation were developed.

* Corresponding author, *E-mail address*: gkovtun@kipt.kharkov.ua

2. Analysis of the behavior of impurity elements in cadmium and lead

The basis for the method of metal purification is the difference in the compositions of a separated mixed liquid and a vapor formed from it. This difference is characterized by the value of relative volatility α of the component to be separated (with reference to the purification process this value is named as a separation factor). For the case of a diluted ideal solution the expression determining the ideal impurity separation factors α_i upon molecular evaporation is given in [5]. The calculated values of ideal impurity separation factors α_i for cadmium in the temperature range from 600 to 900 K are given in [3]. For lead the same calculations were performed. For calculations the values of element vapor elasticity taken from [6] were used.

The determined values of ideal impurity separation factors α_i in Cd and Pb in the temperature range from the melting point to the boiling point have shown that the spectrum of impurity elements includes light volatile impurities ($\alpha_i << 1$), heavy-volatile impurities ($\alpha_i >> 1$) and several impurities with $\alpha_i \sim 1$, belonging to the difficult-to-remove impurities. For harmful impurities in the scintillation detectors, the number of purification repetition, calculated by α_i values, is 100 and more that implies an effective purification of cadmium and lead from these impurities by vacuum distillation.

The results of calculations on the behavior of impurity elements in the process of Cd distillation are given in [2, 3]. Investigations were carried out on the dependence of the efficiency of Cd melt purification from the light volatile impurities on the residue fraction and the dependence of the efficiency of Cd condensate purification from the heavy-volatile impurities on the distillation efficiency at a given temperature. Analysis of the dependences has shown that more than 10 purifications of the melt from light volatile impurities with $\alpha_i << 1$ will occur upon evaporation of Cd < 10 %. For the heavy-volatile impurities with $\alpha_i >> 1$ more than 10-fold purification of the condensate will occur upon Cd refining to the condensate of > 95%.

So, for the deep purification of Cd and Pb more preferable can be realization of the process of step-by-step purification from light-volatile and heavy-volatile impurities with wastes of basic metal (10-15%) that has been earlier realized for natural cadmium refining [3]. To provide minimal losses of initial materials, in particular ^{106}Cd, for the given case we have chosen, instead of the step-by-step purification, a method consisting in the combination of prefiltration and distillation with subsequent casting of distillates in the form of measured ingots.

The obtained results of calculations of the efficiency of cadmium and lead refining were taken into account in the development of improved distillation devices and in the choice of temperature and time regimes of distillation purification processes.

3. Experimental investigation of the processes of purification of natural Cd, enriched ^{106}Cd and archaeological Pb by vacuum distillation

3.1. Materials and methods of purity control

The initial materials for purification were granular Cd of ChDA grade (spec 6-09-3095-78), enriched ^{106}Cd and archeological Pb.

To exclude the ingress of background impurities into the metal being refined in the purification processes we used high-purity accessory materials and equipment. A crucible and a condenser of distillating apparatuses are made of high-purity graphite of MPG-7 grade, and a heater, heater components and screens are made of the spectrally pure graphite, corresponding to spec 48-20-90-82. The content of regulated impurities in such graphite is $\leq 6.2 \cdot 10^{-4}$ mass %. An inert atmosphere for filtration of Cd and ^{106}Cd was the highest-grade argon gas corresponding to the State Standard 10157-88 with an argon volume fraction no less than 99.995%.

Quantitative analysis of samples determining the impurity content in the initial and refined metals was performed by the ICP-MS and AAS methods (chemical laboratory of LNGS, Assergi, Italy), as well as by the LMS method (NSC KIPT, Kharkiv, Ukraine). The AAS method was used

mainly to determine the iron content in cadmium, as the Fe concentration measured by the ICP-MS method was too high. It is because the iron isotopes are overlapped with the isobaric interference from the ^{58}Ni isotope and doubly ionized ^{112}Cd and ^{114}Cd. The accuracy of impurity content determination by the above-mentioned methods is 15…30%.

3.2. Experimental procedure, results and discussion

To develop the process of deep refining of ^{106}Cd with minimal losses and a high product yield, we carried out preliminary investigations with natural cadmium. For this purpose a distillating apparatus and a filtrating apparatus providing condensate casting in measured ingots with an initial metal charge to 250 g were developed and fabricated. The crucible and the condenser of this distillating apparatus are interchangeable that permits to repeat distillation without removing the distillate from the condenser.

The process of high-purity cadmium production consisted in the following. The initial cadmium (about 200 g) with an initial impurity content (Table 1) was preliminary filtered, to minimize losses, in the pure argon atmosphere under pressure in the apparatus chamber ~ 120 kPa. As a result of filtration, oxides of impurity metals and slag in the form of a film remained on the surface of filtrating apparatus plate. Then the chamber was evacuated and in the process of refining the pressure in it was maintained as 10^{-3} Pa or lower. Cadmium, preliminary refined by filtration, was subjected to two distillations with a distillation fraction more than 98% in each process. During the process cadmium was evaporated at 630…650 K and condensed at 530…550 K.

Condensation at such temperatures leads to the partial purification of the condensate from the light-volatile impurities (Na, K, S, P, As, Se etc.) by removing them into the chamber volume through the little hole in the condenser. The heavy-volatile impurities (Fe, Ni, Co, Si, Cu, Al, Au, Ag, Pb, Tl, Sb, Bi, Li, Sn, Mn etc.) were concentrated in the residue in the crucible. After refining by distillation, cadmium was cast in the measured ingots. The similar procedure was used for refining ^{106}Cd with 2…5 distillations depending on the degree of purity of the initial material.

Table 1. Impurity composition of natural Cd and enriched ^{106}Cd before and after purification.

Impurity element	Concentration in natural Cd (ppm)		Concentration in ^{106}Cd (ppm)	
	before purification	after purification	before purification	after purification
Ni	30*	0.3* / ≤ 0.2**	0.6*	0.6* / ≤ 0.2**
Cu	47*	0.3* / ≤ 0.2**	5*	0.7* / 0.5**
Fe	0.4***	0.17*** / ≤ 0.5**	1.3***	0.4*** / ≤ 0.4**
Mg	30*	≤ 0.5* / ≤ 0.05**	12*	≤ 0.5* / ≤ 0.05**
Mn	0.2*	0.1* / ≤ 0.3**	0.1*	0.1* / ≤ 5**
Cr	0.2*	0.1* / ≤ 1**	9*	≤ 0.5* / ≤ 0.1**
V	<0.005*	≤ 0.005* / ≤ 0.08**	<0.005*	≤ 0.01* / ≤ 0.08**
Co	0.3*	≤ 0.003* / ≤ 1**	0.02*	≤ 0.01* / ≤ 0.1**
K	8*	≤ 5* / 0.7**	11*	≤ 10* / 0.04**
Pb	1000*	3* / ≤ 1**	270*	8* / ≤ 0.3**
Th	<0.001*	≤ 0.001*	<0.001*	≤ 0.001*
U	<0.001*	≤ 0.001*	<0.001*	≤ 0.001*

* ICP-MS – Inductively Coupled Plasma - Mass Spectrometry analysis
** LMS – Laser Mass Spectrometry
*** AAS – Atomic Absorption Spectroscopy

For purification of archeological lead by vacuum distillation, a special apparatus was developed providing the metal vapor condensation into the liquid phase with a high efficiency and high product yield > 95%. Surface contaminations, metal oxides and slag, similarly as for cadmium, were removed by prefiltration of the initial metal. Then the metal was placed in the crucible and

heated to working temperatures (~ 1220 K), and, as a result, it was evaporated and passed into the condenser. During the distillation process the lead was purified from the heavy-volatile impurities (Mn, Ni, Co, Cu, Fe, U, Th etc.), and the light-volatile impurities (Ca, Mg, Tl, K, As etc.) were removed through the special hole due to the high temperature (~ 1020 K) in the condenser. After that the pure metal was formed in ingots in the casting device.

The impurity concentration in archeological lead (Table 2) was determined by the LMS method. Analysis of the impurity composition shows a good purification of Pb from Ni, Cu, Zn, Ag, Sb and other impurities.

Table 2. Impurity composition of archaeological lead before and after purification.

Impurity element	Before purification, ppm	After purification, ppm	Impurity element	Before purification ppm	After purification, ppm
Mg	0.09	< 0.04	Cu	**6.3**	< 0.1
K	0.5	0.35	Zn	**2.6**	< 0.2
Ca	0.56	0.3	As	< 0.1	< 0.1
V	< 0.07	< 0.07	Ag	**34**	< 0.6
Cr	< 0.09	< 0.09	Sb	**5.4**	< 0.6
Mn	< 0.08	< 0.08	Tl	< 0.8	< 0.8
Fe	< 0.09	< 0.09	Bi	< 1	< 1
Co	< 0.09	< 0.09	Th	< 0.7	< 0.7
Ni	< 0.2	< 0.09	U	< 0.7	< 0.7

Analysis has shown that the residue after filtration in the form of oxide film is enriched with separate impurity elements. So, in this case, similarly to the case of cadmium, filtration serves as an additional purification element.

Comparative analysis of the obtained results evidences that the refining by vacuum distillation in combination with filtration is an effective method of deep purification of cadmium and lead. The purification procedure under consideration provides for several impurities more than 100-fold decrease of their content – to the level required for a material used in fabrication of scintillators (Cd,^{106}Cd,Pb)WO_4 and (Cd,^{106}Cd,Pb)MoO_4. Also, a high product yield (> 96%) is reached and irreversible losses are decreased. It has been found that the highest efficiency of purification takes place after the first distillation. Depending on the initial material purity, the required purity level, under similar distillation conditions, is reached by repetition of the distillation process.

In Fig. 1 presented are the samples of high-purity ingots of ^{106}Cd and archeological lead after filtration, distillation and casting.

4. Conclusions

Based on the analysis of earlier calculations of the behavior of impurity elements in metals in the process of their purification with the distillation procedure, the methods and devices were developed for deep purification of Cd, ^{106}Cd and Pb. A combined effect of filtration and distillation on the deep purification from harmful impurities was investigated in experiments. The use of the complex process for purification of Cd, ^{106}Cd and Pb provides more than 100-fold purification from harmful Ni, Cu, Mg, Co, Fe and radioactive impurities. As a result of investigations, the pilot batches of high-purity Cd, ^{106}Cd and Pb with a product yield > 96% and irreversible losses < 1%, applicable for production of high-quality scintillators (Cd,^{106}Cd,Pb)WO_4 and (Cd,^{106}Cd,Pb)MoO_4 were obtained.

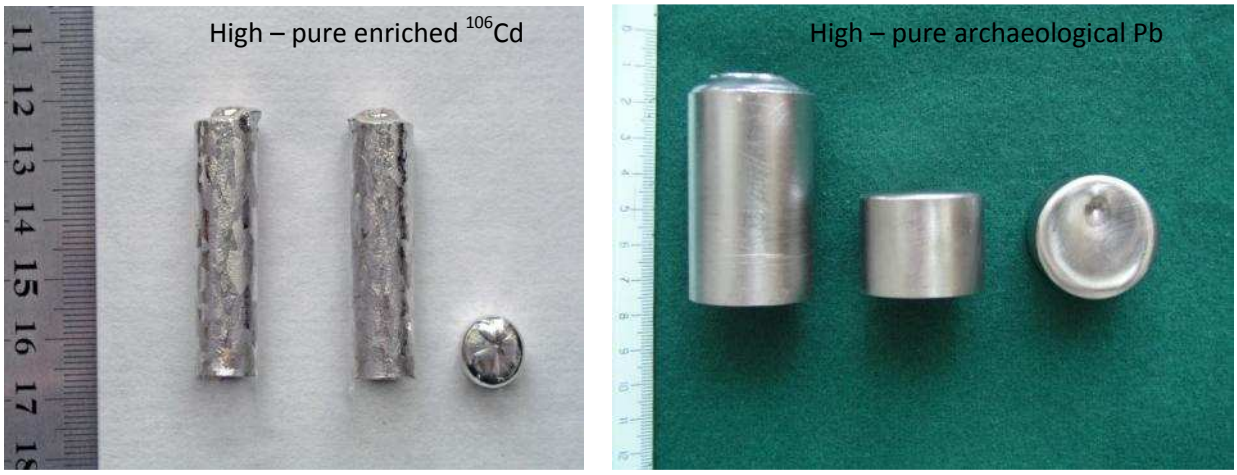

Fig. 1. Ingots of high-purity ^{106}Cd and archaeological Pb.

References

1. L.F. Kozin, E.O. Berezhnoj, K.L. Kozin, High-Purity Materials 5 (1996) 11.
2. G.P. Kovtun, A.I. Kravchenko, A.P. Shcherban', Technology and Designing in Electronic Equipment 3 (2001) 6.
3. G.P. Kovtun, A.P. Shcherban', Visnyk of Kharkiv Nat. Univ., ser. phys. "Nuclei, Particles, Fields" 642/3/25 (2004) 27 (in Russian).
4. G.P. Kovtun, A.P. Shcherban', Patent 1246, Ukraine, C22B9/04, C22B9/187. National Science Center "Kharkov Institute of Physics and Technology" – № 2001075474; Appl. 31.07.01; Published. 15.05.02, Bulletin 5 (2002) 3.
5. V.A. Pasukhin, A.Ya. Fisher, *Separation and Refinement of Metals in Vacuum*. Moscow, Metallurgiya, 1969, 203 p. (in Russian).
6. A.N. Nesmeyanov, *Vapor Pressure of Chemical Elements*, Moscow, Publ. of Ac. Sci. USSR, 1961, 396 p. (in Russian).