

Purification of cadmium by selective volatilization in vacuum in presence of oxide phase on its melt

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Abstract. Purification of cadmium in the presence of a thin (~ 0.001 mm) oxide layer on the surface of the molten metal was carried out using a simple system designed and fabricated locally. The analytical results revealed that the distillation through oxide layer gave better separation for Co, Ni, Cu, Zn, Ag, Sn, Hg and Tl, when compared to the distillation without oxide layer. This was attributed due to the impurity metal oxide phases formation on the surface of the molten metal. The influence of oxygen flow time on the distillation rate of cadmium was established. There was no excess oxygen (O) retained in the distillate after two consecutive vacuum distillations through oxide route. The experiments were conducted at the level of nearly 1.5 kg a batch to study the impurities behaviour due to upscaling. The detailed chemical analysis of 58 impurity elements in Cd in presence and absence of oxide layer was carried out by glow discharge mass spectrometry (GDMS).

Keywords. High purity; cadmium; selective evaporation; oxide layer; glow discharge mass spectrometry.

1. Introduction

The extreme purities in individual metals is motivated by the theoretical limitations of separating the impurities and practical importance of determining the intrinsic physical properties. One part of impurity in the million of a matrix metal can significantly influence the physical properties (Kinchin *et al* 1981; Capper 1982; Murarka *et al* 1993; Keksi 2002). Preparation of high purity metals demands a combination of different chemical and physical refining methods (Safarzadeh *et al* 2007). As the degree of refinement increases to higher levels, purification methods are predominately based on physical processes like vacuum distillation, crystallization, diffusion, electro-migration, etc, (Singh *et al* 1968). The distillation at batch scale requires considerable control of experimental parameters, which can play an important role in the separation of ppb/ppt level impurities.

The basis for vacuum distillation technique is separation of impurities during evaporation followed by condensation of a relatively pure part owing to the difference in vapour pressure and controlled by separation coefficient of impurities in the vapour phase. Comparison of experimental data on impurity distribution coefficient in melt–solid and separation coefficients in melt–vapour phases (Devyatkin and Eliev 1982), suggest that the latter method is preferred due to simple equipment and reduced process time. Under volatilization conditions in vacuum, the most difficult impurity to separate is Zn in Cd due to its separation coefficient of two

(Kovalevski *et al* 1996). It was reported that by adding metal oxide phases, a considerable change in the physico-chemical behaviour of several impurities can occur during purification (Kovalevski *et al* 1996). The main principal is the oxidized part of cadmium (CdO) which extracts impurity from the melt as an oxide A_rO_s , where ‘A’ represents impurity element, r and s are the respective valences. The impurity distribution between the phases is assumed to be homogeneous in composition and determined by thermodynamic equilibrium. At equilibrium the reaction looks like $rA + sCdO \leftrightarrow A_rO_s + sCd$, at a partial pressure P_i^0 and temperature of evaporation, T (K) (Ali *et al* 2004).

The purification work as was reported by Kovalevski *et al* (1996), was carried out using 1.5 to 1.8 kg of input material and distillation was carried out in a quartz tube. Normally these kind of experiments have to be conducted at kilogram level in order to harvest the R&D into technology and later on upscale to a required batch scale of production. The grams scale also will give similar results, because, the separation of impurities depends on partial pressures of individual metal impurities with respect to parent matrix element. In this case the matrix element is cadmium. However, the equipments for purification used by Kovaleski *et al* (1996) were quartz tubes and graphite boats. Also, the impurities analysed shows higher detection limits (percentages), probably due to the higher limit of quantification (LOQ) of the analytical equipments used.

In order to adopt this technique into practice, one has to demonstrate the purification process, with suitable materials of construction of the equipment, because, in our experience, quartz tube breaks with CdO and SiO₂ (quartz) reaction during

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cooling and heating cycles due to thermal expansion differences. Hence, a simple design using stainless steel retort and graphite crucible for collection was adopted.

This piece of work deals with the simple equipment constructed using locally available materials for purification which circumvents the use of expensive and imported quartz tubes. All the results were analysed using glow discharge mass spectrometry (GDMS) available at the National Research Council (NRC), Canada. GDMS technique is the most suitable analytical tool for the quantification of parts per billion (ppb)/parts per trillion (ppt) level impurities in high purity material matrices and compound semiconductors, because, it adopts no chemicals in sample preparation. In view of this, we have separately given these results and compared the extent of separation of impurities with and without oxide layer on cadmium melt.

The purity achieved by distillation through oxide phase at a batch scale and detailed impurity analysis by GDMS has not been reported in the literature. Variation in the mass to be purified is expected to change the purification process parameters considerably. We report in this paper a comparative study on the purification of cadmium through normal vacuum distillation and distillation through oxide layer and detailed impurity analysis using GDMS for nearly 58 impurity elements in Cd matrix.

2. Experimental

The details of vacuum distillation assembly are given in figure 1. The metal evaporator and collector system essentially consisted of two cylindrical crucibles made up of isotropic fine grain high density graphite (R-7340) inverted over

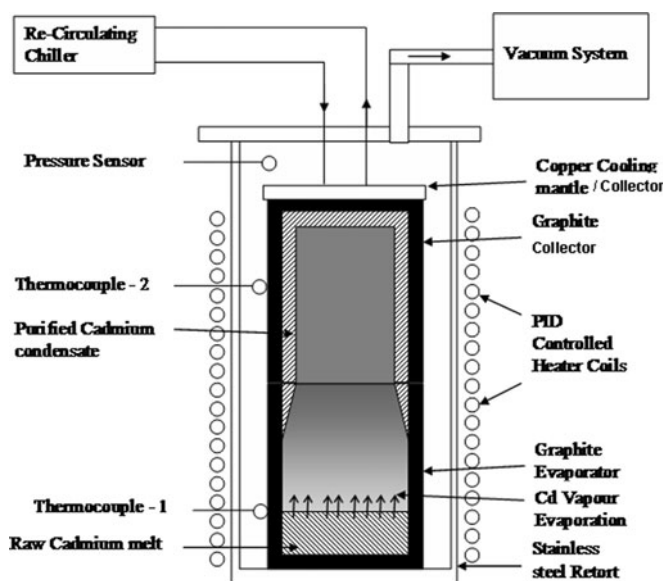


Figure 1. Schematic diagram showing components distillation assembly.

one on the other. A copper cooling jacket was placed on the top of the crucible which acted as a condenser. A cup shaped graphite filter (3 Φ filter holes) had dimensions of 60–100 (OD) \times 150 (H) \times 10 (T) Φ , where 60 and 100 were bottom and top OD, respectively and H and T were height and thickness, respectively. Similarly, the collector had the dimensions of 100–120 (OD) \times 200 (H) \times 8 (T) Φ and evaporator had the dimensions of 100–120 (OD) \times 310 (H) \times 8 (T) Φ . The entire assembly was placed in a stainless steel (SS316) retort connected to a vacuum system. This SS retort was placed in a heating furnace with a provision to control the temperature within $\pm 5^\circ\text{C}$. The system was dynamically maintained at a vacuum of nearly 2×10^{-5} torr before starting the melt evaporation and nearly 2×10^{-4} torr during the distillation process.

2.1 Vacuum distillation of cadmium

The commercial grade cadmium (99.9 at.%) was filtered to remove excess oxides by melting in the filter assembly under a dynamic vacuum. The darkish brown coloured residue indicated the presence of excess copper and other metal oxides. Elemental analysis of the residue using inductively coupled plasma optical spectrometry (ICPOES) showed the accumulation of Pb and Cu to the extent of 230 and 210 ppm, respectively.

Nearly 5 kg of filtered cadmium was loaded into the bottom graphite crucible. After fixing the top crucible and cooling jacket, the temperature was increased to 200°C to remove any moisture under a dynamic vacuum of nearly 10^{-5} torr. Subsequently, the high vapour pressure impurities were removed at a temperature 50°C below the distillation temperature, under the same pressure conditions. After 15 min of time, the collection chamber was replaced with a freshly cleaned third graphite crucible and the experiment was repeated at a temperature 70°C above the melting point of cadmium. After 2 h of distillation, the furnace was cooled to room temperature (RT). The SS retort was opened after flushing with inert Ar-gas for a couple of times to remove any trapped gases. Finally, the distillate was removed by sliding down the crucible. The samples were cut from the hat at different places for analysis. This hat shaped cadmium was subsequently cut into pieces of nearly 1 inch size and loaded into a freshly cleaned graphite crucible. In other words, the purified distillate from the first stage was used as an input material for the second stage. The second stage vacuum distillation was repeated by adopting similar experimental procedure as that of first stage.

2.2 Vacuum distillation of cadmium through oxide layer

Similarly, in a separate experiment, about 0.9 kg of filtered cadmium was oxidized with a predetermined oxygen flow rate of nearly 40 SCCM for 30 min using mass flow meter (Bromkhost high-tech type E-7600-AAA). The duration of time was selected based on series of distillation experiments

with variable oxide formation time. The thickness of the CdO layer was estimated microscopically after taking a transverse section of the top portion of the ingot, polishing the piece and taking the image. The thickness was measured to be around 0.001 mm. The distillation experiment was repeated for various times in the same manner as described above.

2.3 Sample preparation and analysis

High pure cadmium sample of 0.5 g each was dissolved in a 5 ml sub-boiled nitric acid in a 25 ml teflon beaker. The solution was fed to inductively coupled plasma emission spectrometer (ICP-OES), and inductively coupled plasma mass spectrometer (ICPMS). The grease, if any, during handling of the cadmium sample was cleansed by shaking in 1% sub-boiling nitric acid for 1 min. The matrix separation of cadmium was also carried out on some batches for the analysis on ICPMS. The results analysed using ICPOES were taken only to establish the effectiveness of purification process for specific impurities in case of oxide layer formation on cadmium. However, detailed results on cadmium purification on similar experiments were published elsewhere from this laboratory (Munirathnam *et al* 2005; Ali *et al* 2006, 2007). The cadmium distillates from the 1st and 2nd stages of vacuum distillation in presence and absence of oxide layer were analysed by GDMS at the National Research council (NRC), Canada.

3. Results and discussion

The distillation rate of cadmium in g/h was plotted against the oxide layer formation time (min) and is shown in figure 2. These experimental results of distilled cadmium revealed that the rate of distillation as a function of distillation time decreased exponentially with the increase in oxide concentration on the cadmium melt surface, at least up to 40 min. The weight of input material quantity, oxide layer forma-

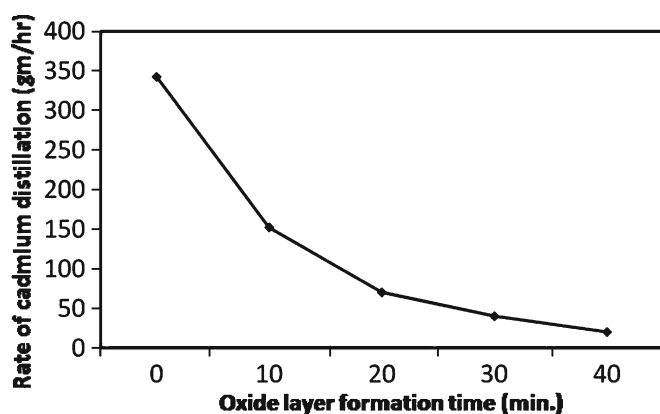


Figure 2. Variation of cadmium distillation rate (g/h) with oxide layer formation time (min).

Table 1. Rate of distillation of cadmium as a function of oxygen flow rate onto Cd melt.

Sl. no.	Input cadmium (g)	Oxygen layer formation time (min)	Rate of distillation of cadmium (g/h)
1	845	With out oxide layer	342
2	847	10	152
3	885	20	70
4	880	30	40
5	860	40	20

tion time and rate of distillation (g/h) are shown in table 1. The oxide film thickness was calculated to be nearly equal to 0.001 mm at 30 min of oxygen flow @40 SCCM. Zinc impurity analysis on ICPOES revealed that its concentration in Cd distillate decreased exponentially from 600 ppm to 290 for 10 min of oxide layer formation and then it almost stabilized after 30 min of oxide layer formation. In other words, further increase in oxide layer thickness beyond 0.001 mm had no significant change in the separation of Zn from Cd. This was ascribed due to the formation of thermo-dynamical equilibrium for the separation of Zn in Cd.

Based on the behaviour of impurities during cadmium purification, it was expected that the impurities such as Cu, Ag, Au, Pb, S, Bi, Co, Ni, Pt should remain in the evaporator in the form of solution in Cd while Li, Na, Be, Mg, Ca, Zn, Sr, Ba, B, Al, Sc, Ga, Y, In, La, Si, Ti, Ge, Zr, Sn, Hf, V, Nd, Ta, Cr, Mo, W, Mn, Fe should remain in the oxide phase (Keksi 2002). This implies that Zn impurity was expected to remain in the oxide phase. Detailed GDMS analytical results of 58 impurity elements from the first and second distillations through oxide phase from is shown in table 2.

3.1 Behaviour of C, N and O impurities

The carbon (C), nitrogen (N) and oxygen (O) impurities in input cadmium were 900, 110 and 4300 ppm, respectively. These were increased to 4000, 2800 and 7600 ppm after first distillation. This was attributed primarily due to the unforeseen contamination from the adsorbed surface oxides dissolved into the melt. After subsequent 2nd vacuum distillation, C, N and O in Cd were reduced to 2500, 640 and 2200 ppm, respectively. On the other hand, after oxidation and 1st distillation, C, N and O impurities in Cd increased to 4200, 760 and 99000 ppm and after subsequent 2nd vacuum distillation, they were reduced to 1700, 690 and 2800 ppm, respectively. Although the content of O was higher after the 1st distillation due to the oxide layer formation, the Cd distillate after 2nd distillation contained relatively comparable contents of C, N and O in Cd. This indicated that by distilling through oxide phase there was no difficulty of excess oxygen after two consecutive distillations. In addition, appreciable gain in the separation of metallic impurities would be an added advantage.

Table 2. GDMS analytical results of vacuum distilled cadmium. Cd-RM is input material, Cd-1 is after 1st vacuum distillation, Cd-2 is after 2nd vacuum distillation, Cd-O-1 is after 1st vacuum distillation in the presence of oxide layer and Cd-O-2 is after 2nd vacuum distillation in the presence of oxide layer.

Impurity	(mass ppb)										
	Cd-RM	Cd-1	Cd-2	Cd-O-1	Cd-O-2	Impurity	Cd-RM	Cd-1	Cd-2	Cd-O-1	Cd-O-2
Li	<7	<5	<11	<9	<7	Br	<8	<8	<15	<6	<7
Be	<2	<1	<2	<1	<1	Rb	<0.4	<0.3	<1	<0.4	<0.4
B	<2	5	11	<2	2	Sr	<0.4	<0.2	<1	<0.2	<0.3
C	900	4000	2500	4200	1700	Y	<0.3	<0.2	<0.5	<0.3	<0.3
N	110	2800	640	760	690	Zr	<0.3	<0.3	<0.5	<0.5	<0.3
O	4300	7600	2200	99000	2800	Nb	<0.4	<0.3	<1	<0.4	<0.4
F	<4	<1	<5	<1	<2	Mo	<1	<1	<2	<0.9	<0.9
Na	49	7	97	20	<3	Pd	NA	NA	NA	NA	NA
Mg	<3	<1	<3	<2	<2	Ag	7400	<40	<25	<25	<8
Al	<2	<2	<2	5	<1	Cd	Matrix	Matrix	Matrix	Matrix	Matrix
Si	4	14	45	19	7	In	<20	<45	<45	<120	<25
P	<1	<1	<2	<1	<1	Sn	57	<15	<25	<7	<8
S	87	5	<5	5	<2	Sb	290	<2	<2	<1	<0.9
Cl	5	26	67	44	8	Te	<35	<90	<30	<85	<55
K	<1	<2	<10	<4	<1	I	<20	<15	<130	<75	<75
Ca	<10	<8	<40	<10	<10	Cs	<3	<3	<10	<9	<6
Sc	<0.6	<0.4	<0.9	<0.5	<0.5	Ba	<8	<5	<30	<8	<12
Ti	<0.3	<0.9	<0.5	<0.3	<0.3	La	<3	<65	<15	<25	<20
V	<0.2	<0.2	<0.3	<0.2	<0.2	Ce	<6	<11	<25	<45	<30
Cr	<1	<0.8	<3	<1	<1	Hf	<0.3	<0.3	<0.5	<0.2	<0.3
Mn	<20	<20	<20	<20	<20	Ta	NA	NA	NA	NA	NA
Fe	<15	<15	<15	<15	<15	W	10	15	<1	<0.8	<0.6
Co	1000	<0.3	<0.7	<0.2	<0.2	Pt	<0.6	<0.5	<1	<0.5	<0.6
Ni	27000	10	20	<3	<2	Au	<5	<5	<5	<5	<5
Cu	570000	190	330	33	<2	Hg	110	40	32	<10	<5
Zn	78	57	130	<4	<4	Tl	9800	6	18	67	0.8
Ga	<1	<0.9	<2	<1	<1	Pb	480000	130	110	36	<0.7
Ge	<3	<2	<4	<2	<2	Bi	19	<0.4	<0.7	<0.4	<0.4
As	<10	<10	<10	<10	<10	Th	<0.6	<0.5	<0.9	<0.9	<0.8
Se	<15	<25	<25	<6	<25	U	<0.09	<0.06	<0.1	<0.08	<0.08

NA =Not analysed

3.2 Separation of metallic impurities

Cadmium purification results with and without oxide layer showed substantial reduction of zinc impurity in cadmium distilled with oxide layer. On the other hand, without the oxide layer, the Zn in Cd was reduced from 2 ppm after first distillation and then to 0.4 ppm after subsequent second distillation (Ali *et al* 2004). In the present work, Zn in Cd was reduced from 78 to 57 ppb after first distillation in the process where there is no oxide layer and to <4 ppb after first distillation through oxide phase. The basic reaction mechanism was $rA + sCdO \leftrightarrow A_rO_s + sCd$, where 'r' is the number of impurity atoms of 'A' to be separated and 's' the number of CdO molecules or cadmium atoms. During the process of purification, the most difficult impurity to remove is zinc, because of its distribution coefficient in melt–vapour systems, which is 2 (Kovalevski *et al* 1996). It was also demonstrated

that the behaviour of the physico-chemical system used in purification by adding new phases changes the behaviour of several impurities. Hence, in this case by introducing CdO into the system essentially influences the results of purification of impurities with greater affinity to oxygen than cadmium. This class of impurities includes zinc in addition to others (Shelpakova *et al* 1993). The other impurities like Mg, Al, Fe, Cu, Pb, Ag, Co, Ni, Sb, Bi have also been reduced by nearly two orders. The results tabulated in table 2 also indicated that the degree of separation of Ni, Cu, Zn, Ag, Sn, Hg and Tl were higher during distillation through oxide layer, when compared to without oxide layer. It was also observed during experimentation that the rate of distillation decreased from 350–400 g/h (without oxide film) to 125–150 g/h (with oxide film). This indicated a mesh like behaviour of oxide layer on the cadmium melt by retaining the metal oxides and allowing the metal to evaporate.

4. Conclusions

The following are the major conclusions:

- (I) The experimental system designed and fabricated with all indigenous components can distill cadmium up to 6N (99.999 at%.) purity at batch scale.
- (II) The zinc in cadmium reduced drastically from 78 ppb to <0.4 ppb in the presence of oxide layer, which otherwise was difficult to remove due to separation coefficient in melt vapour system close to 2.
- (III) The impurities like C, N and O reduced considerably during second distillation in the presence of its oxides.
- (IV) Significant reduction in Co, Ni, Cu, Sn, Sb, Hg, Tl and Pb in Cd was observed due to the presence of small amount of metal-oxides on the molten surface during vacuum distillation.
- (V) The results can be effectively used to enhance the design for higher capacities of cadmium distillation using novel purification of cadmium metal through oxide phase and the purification of cadmium at a higher batch scale without sacrificing the purity required.

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