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The behaviour of impurity in the purification of high purity magnesium via vacuum distillation

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Table S1 shows the evaporation constant data for the relationship between the equilibrium vapor pressure and temperature.

Table S1. The equilibrium vapour pressure constants of some elements.

Elements	A	B	C	D	*T*/K
Al	−16380	−1.0	/	14.445	933~2793
Ca	−9350	−1.39	/	14.94	298~1112
Cu	−17770	−0.86	/	14.42	298~1358
	−17520	−1.21	/	15.335	1358~2836
Fe	−21080	−2.14	/	19.02	298~1811
	−19710	−1.27	/	15.395	1811~3135
Mg	−7780	−0.855	/	13.54	298~923
	−7550	−1.41	/	14.915	923~1363
Mn	−14920	−1.96	/	18.32	298~1517
	−14520	−3.02	/	21.365	1519~2335
Ni	−22500	−0.96	/	15.72	298~1728
	−22400	−2.01	/	19.075	1728~3187
Pb	−10130	−0.985	/	13.285	600~2023

Zn	−6850	−0.755	/	13.36	298~693
	−6620	−1.255	/	14.465	693~1180

Table S2 shows the solubility results calculated via "Equilib" module in the FactSage 8.0 software.

Table S2. The solubility results calculated via the FactSage 8.0 software.

Impurities	Setting concentration (ppm)	Solubility (%)				
		848 K, 18 Pa	873 K, 85 Pa	923 K, 100 Pa	973 K, 140 Pa	1023 K, 400 Pa
Zn	19	0.2551	0.1701	/	/	/
Ca	27	0.2775	0.3127	0.4089	0.6166	/
Pb	17	0.8418	0.5669	/	/	/
Al	415	0.1424	0.0927	/	/	/
Cu	1.9	0.2243	0.1508	/	/	/
Ni	0.44	0.3585	0.3983	0.4961	0.6373	0.9181
Mn	137.5	/	/	0.0036	0.0252	0.0326
Fe	13.1	/	/	0.0003	0.0005	0.0008

The surface of the ingot (99.9% pure Mg) was initially cleaned mechanically by a milling machine to remove the oxide layer. The ingot was then cut into cubes and the surfaces of these cubes were mechanically grinded by Al_2O_3 sand papers to get rid of the cooling fluid (needed during cutting) and surface contamination. Finally, these tubes were immersed in ethanol for a 3-hour ultra-sonic bath to prevent foreign contaminants that may come from the sandpapers.

The heat source of the system is generated from a coil of a vacuum induction furnace (40 kW maximum power, 4 kHz maximum frequency, 1873℃ maximum temperature). The reaction device is constructed of two parts made of steel and graphite. Steel was chosen for the upper part, as graphite was too fragile and would be broken while recovering the refined Mg crystals after each trial. The appearance of the assembled setup is shown in Figure S1. All parts of the setup contacting with magnesium during the trials except for graphite lid and graphite crucible were covered with special coating based on yttrium oxide, diluted with distilled water. The whole setup was completely wrapped in thermal insulation layer to minimize energy loss, which was essential for two reasons: 1) prohibited the Mg condensation in the aperture and increased the temperature of the condenser, thus decreasing the temperature gradient between the Mg vapour and the condenser. 2) This gradient decrease significantly prohibited the formation of powdery Mg in the condenser, which would be very problematic to collect, as it was highly reactive and prone to burning. Even in case of no accidents occurring during collection, these powders tend to oxidize rapidly, with these oxides present in any formed parts from powdery Mg as harmful non-metallic inclusions. Depending on the temperature and holding time of each trial, the condenser could reach temperatures higher than the melting point, thus triggering the phase change of the condensed material from solid to liquid, with the liquid droplets falling to be collected in the collecting bowl as bulk material.

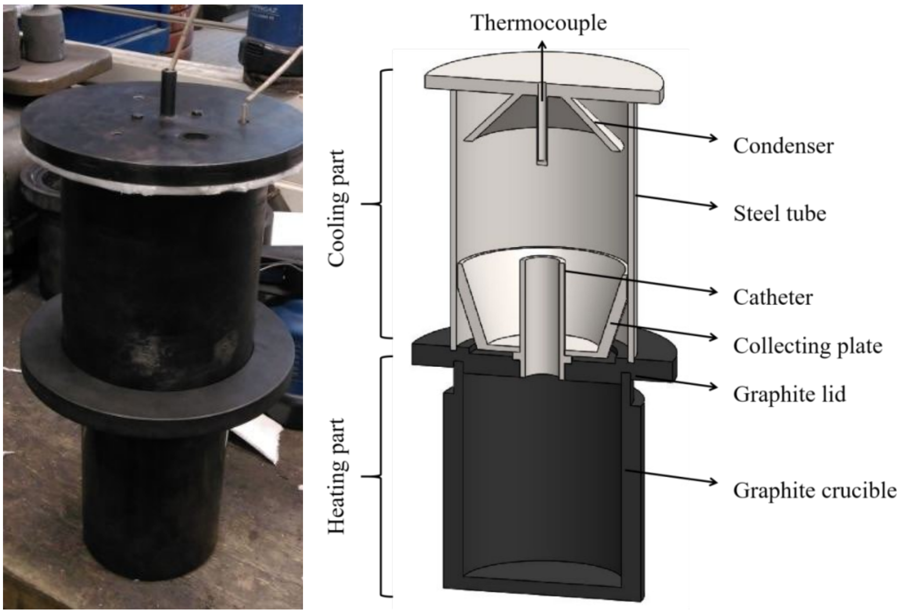

Fig. S1. The actual external view (left) and the cross-sectional view simple sketch (right) of the vacuum distillation setup.

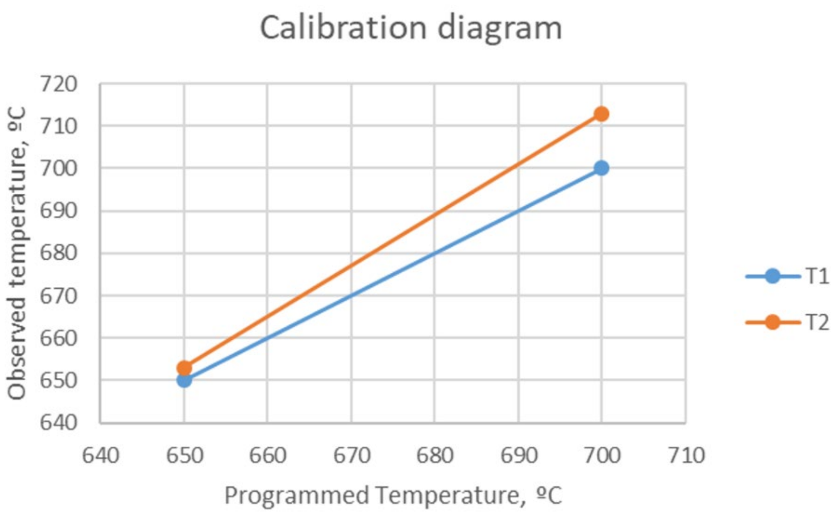

Fig. S2. The relationship between setting temperature and observed temperature.

There were two tests conducted to understand the difference between temperature inside the crucible full of molten magnesium and the temperature of the crucible bottom. Figure S2 shows the result of the temperature calibration. T1 was the thermocouple near the bottom of the crucible, and the T2 thermocouple was placed in the molten magnesium. It can be seen that the difference value increased as the temperature. The final temperature data were based on the calibration difference. In addition, the device was covered by a heat-insulating material to better save heat inside the device and prevent the evaporated magnesium from flowing out of the crucible. After reaching the heating temperature, the condenser remains stable for a period of time, which we regard as the condensation temperature of the experiments. The parameters and data for all trials are listed in Table S3.

Heating temperature (K)	Holding time (min)	Pressure (Pa)	Steam jet temperature (K)	Evaporation ratio (%)	Loss ratio (%)	Recovery ratio (%)
848	120	18	748	26.613	-0.423	101.59
	150		790	29.037	0.022	100.61
	180		757	34.527	-0.489	101.42
873	120	85	843	28.086	0.022	99.92
	150		780	33.889	-0.089	100.26
	180		763	37.912	-0.846	102.23
923	30	100	794	21.429	-0.223	101.04
	45		783	27.313	0.220	99.19
	60		860	43.049	1.570	96.35
	90		876	60.352	0	100
973	30	140	830	40.444	1.556	96.15
	45		813	58.482	0.670	98.86
	60		873	77.578	2.009	97.98
	90		912	95.721	4.260	95.72
1023	30	400	860	50.661	0.220	99.57
	45		867	60	1.111	98.15

	60	913	82.667	0.222	99.73
	90	893	96	4.222	95.60

Table S3. Data of all vacuum distillation experiments.

Table S4. The comparison of experimental parameters and impurity concentrations of Mg in vacuum distillation process published by different researchers.

Ref.	Initial Mg (g)	T_{heat} (K)	T_{cond} (K)	P (Pa)	Before or after V.D.	Impurity concentration (ppm)					
						Zn	Mn	Al	Cu	Fe	Ni
[24]	14	873	\	15	B.V.D.	35	97	\	6.4	660	\
					A.V.D.	38	9.9	\	1.8	68	\
[25]	25.53	973	723-773	1.33	B.V.D.	56	17.6	\	3	97	\
					A.V.D.	15-17	0.04	\	0.3	0.07	\
[26]	2500	700-800	630-750	133	B.V.D.	37	156	110	5	24	3
					A.V.D.	25	4.5	3.8	1	4	<0.4
[27]	\	873	633	<1	B.V.D.	<3	20	31	<3	45	<3
					A.V.D.	<3	<1	<1	<3	<3	<3
[30]	45	973	723-873	1.3×10^{-4}	B.V.D.	17	0.02	0.03	0.077	0.54	<0.03
					A.V.D.	5.87	0.041	0.025	<0.01	<0.01	<0.01
[31]	\	1023	973	1.3×10^{-1}	B.V.D.	30	43	23	12	16	3.6
					A.V.D.	1.7	0.02	\	\	\	\
[32]	14.51	1023	\	8×10^{4}	B.V.D.	14.7	68.4	39.4	4.4	21.8	2.6
					A.V.D.	12.4	6	5.4	1	1.2	2.5

This study	450	1023	863-913	400	B.V.D.	13.4	154	277	2	4.93	0.47
					A.V.D.	4.42	0.09	2.85	0.01	0.83	0.01

There are several calculation results of reduction rate that are negative. Considering the very low concentration of trace elements, we consider these to be accidental errors within the acceptable range.

Table S5. Data of all impurity reduction ratio after different vacuum distillation trails.

Temperature (K)	Holding time (min)	Unremoved ratio (%)							
		Zn	Ca	Pb	Mn	Al	Cu	Fe	Ni
848	120	31.34	25.76	9.41	3.51	2.85	15.79	12.33	22.73
	150	31.00	9.44	6.00	0.93	1.16	119.21	15.65	27.27
	180	41.37	16.63	5.21	2.48	1.51	22.37	7.52	12.50
873	120	38.21	19.22	9.62	16.06	3.52	44.47	26.98	14.77
	150	42.26	53.81	4.71	2.60	2.47	21.58	10.73	10.23
	180	46.16	18.94	5.94	6.06	4.99	27.89	13.40	19.32
923	30	13.81	59.09	1.47	1.07	25.58	5.50	74.04	4.26
	45	29.85	61.36	4.41	2.94	36.82	11.00	81.14	10.64
	60	54.48	33.41	11.76	7.79	21.90	6.00	40.57	28.72
	90	80.53	5.56	50.88	55.16	87.95	91.58	102.29	75.00
973	30	108.21	11.91	3.63	0.01	1.08	0.50	26.98	5.32
	45	51.84	2.11	0.53	0.33	0.67	0.53	4.89	2.27
	60	85.82	0.05	0.20	0.12	8.51	0.50	4.97	2.13
	90	43.21	0.04	7.00	1.38	1.18	0.53	5.65	2.27
1023	30	91.04	0.05	2.84	1.47	3.88	4.00	27.99	10.64
	45	32.99	0.05	1.86	0.06	1.03	0.50	16.84	2.13

60	55.45	1.00	0.49	0.03	0.79	0.50	44.62	8.51
90	21.23	13.97	2.50	1.88	29.57	0.43	25.23	2.00
Average *Ui* (minimum in each T)	41.70	12.85	5.95	5.03	5.66	8.76	20.98	6.28