

# Recycling of valuable metals from spent zinc-manganese batteries by vacuum metallurgy<sup>①</sup>

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**Abstract:** At the total chamber pressure of  $1.01 \times 10^{-1}$  Pa, Hg, Cd and Zn were distilled at 773 - 973 K from spent zinc-manganese batteries, Pb was volatilized at 1 173 - 1 273 K while Mn, Cu, Fe and C were remained in the residual.  $\text{MnO}_2$  and ZnO were reduced by carbon in spent dry-batteries at 773 - 1 273 K. Pure metals including Zn, Cd, Hg and Pb were recovered respectively from their mixed vapor by fractional condensation.

**Key words:** spent dry-batteries; recycling; vacuum metallurgy

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## 1 INTRODUCTION

The yield of zinc-manganese batteries is the largest in battery industry in the world because of their low cost. China is the largest country for producing and consuming dry-batteries, produced  $1.7 \times 10^{10}$  pieces of primary batteries and consumed  $7.0 \times 10^9$  pieces in 2 000, about 70% of those were zinc-manganese batteries<sup>[1, 2]</sup>. It was reported that the consumption of Zn,  $\text{MnO}_2$ , Cu and Hg used in battery industry was  $2.5 \times 10^5$ ,  $2.3 \times 10^5$ ,  $4.5 \times 10^3$  and 60 t, respectively<sup>[2]</sup>. However, dry-batteries are usually discarded as wastes after being used, in which contain metals, such as Zn, Mn, Cu, Pb, Cd, Hg, Fe etc, and their compounds. Thus, a large amount of valuable metal resources are wasted and Pb, Cd and Hg also cause serious environmental pollution. Therefore, it has been paid wide attention in the world to recycle useful materials from spent batteries and eliminate pollution to environment.

The main methods for recovering spent batteries are mainly concerned with roasting-leaching, hydro-based leaching and reducing-smelting<sup>[3-15]</sup>. These methods, however, exist some disadvantages, such as complex technological process, more pollution sources, high invest cost, high consumption of energy and raw materials, which results in lower benefit in recycling spent batteries. Because the differences in saturation vapor pressures of Zn, Mn, Cu, Pb, Cd, Hg and Fe in spent batteries at a specific temperature are rather great, it has been proved that it is feasible to recycle these metals respectively by vacuum metallurgical method<sup>[2]</sup>. The disintegrated spent zinc-man-

ganese batteries are heated to certain temperature in vacuum, metals with high vapor pressure are evaporated into gas phase while those with low vapor pressure are remained in residual liquid or residue. The metals in the vapor mixture are separated from each other by condensing at different temperatures to recover valuable metals. The technology can solve many problems existing in conventional method, which shows such advantages as simple technological process, no environmental pollution or low environmental pollution, less floor area and low invest cost, low consumption of energy and raw material<sup>[16]</sup>. The method is of obvious economic and social benefits. Therefore, it is of great importance to study the thermodynamics on recycling useful materials by this method. This paper is aimed at optimizing the operation conditions for the recycling technology from thermodynamic view.

## 2 BEHAVIORS OF COMPONENTS IN SPENT DRY-BATTERIES IN VACUUM

### 2.1 Relationship between vapor pressure of components and temperature

The difference in vapor pressure of each substance in spent dry-batteries at a temperature is the basic principle for recycling spent dry-batteries by vacuum distillation. The components in spent zinc-manganese batteries include Zn,  $\text{ZnCl}_2$ ,  $\text{MnO}_2$ , Cu, Pb, Cd, Hg, Fe, C and so on, most of which are Zn, C, and  $\text{MnO}_2$ . Relationship between saturation vapor pressure of these substances and temperature are listed as following Eqns<sup>[17]</sup>:

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$$\begin{aligned}
\lg p_{\text{Zn}}^* &= -6.850T^{-1} - 0.755\lg T + 10.365 \\
&\quad (298-699\text{ K}) \quad (1) \\
\lg p_{\text{Zn}}^* &= -6.620T^{-1} - 1.255\lg T + 14.465 \\
&\quad (699-1180\text{ K}) \quad (2) \\
\lg p_{\text{ZnCl}_2}^* &= -8.500T^{-1} - 1.50\lg T + 18.735 \\
&\quad (298-599\text{ K}) \quad (3) \\
\lg p_{\text{ZnCl}_2}^* &= -8.415T^{-1} - 5.035\lg T + 28.545 \\
&\quad (599-1005\text{ K}) \quad (4) \\
\lg p_{\text{Mn}}^* &= -14.920T^{-1} - 1.96\lg T + 18.315 \\
&\quad (298-1519\text{ K}) \quad (5) \\
\lg p_{\text{Pb}}^* &= -10.130T^{-1} - 0.985\lg T + 13.285 \\
&\quad (600-2013\text{ K}) \quad (6) \\
\lg p_{\text{Cd}}^* &= -5.908T^{-1} - 0.232\lg T - \\
&\quad 2.84 \times 10^{-4}T + 11.842 \\
&\quad (298-594\text{ K}) \quad (7) \\
\lg p_{\text{Cd}}^* &= -5.819T^{-1} - 1.257\lg T + 14.407 \\
&\quad (594-1050\text{ K}) \quad (8) \\
\lg p_{\text{Hg}}^* &= -3.305T^{-1} - 0.795\lg T + 12.475 \\
&\quad (298-630\text{ K}) \quad (9) \\
\lg p_{\text{Cu}}^* &= -17.770T^{-1} - 0.86\lg T + 14.415 \\
&\quad (873-1356\text{ K}) \quad (10) \\
\lg p_{\text{Cu}}^* &= -17.520T^{-1} - 1.21\lg T + 15.335 \\
&\quad (1356-2843\text{ K}) \quad (11) \\
\lg p_{\text{Fe}}^* &= -21.080T^{-1} - 2.14\lg T + 19.015 \\
&\quad (298-1808\text{ K}) \quad (12)
\end{aligned}$$

The saturation vapor pressure values of substances were calculated at 573–1473 K according to Eqns.1–12, as listed in Table 1.

**Table 1** Relationships between vapor pressure of substances and temperature

$T/\text{K}$	$p_{\text{Hg}}^*/\text{Pa}$	$p_{\text{ZnCl}_2}^*/\text{Pa}$	$p_{\text{Cd}}^*/\text{Pa}$	$p_{\text{Zn}}^*/\text{Pa}$	$p_{\text{Pb}}^*/\text{Pa}$
573	$3.27 \times 10^4$	0.58	5.35	0.21	–
623	$8.88 \times 10^4$	9.28	$3.58 \times 10^1$	1.82	–
673	–	$6.34 \times 10^1$	$1.61 \times 10^2$	$1.13 \times 10^1$	–
773	–	$1.31 \times 10^3$	$1.77 \times 10^3$	$1.89 \times 10^2$	–
873	–	$1.25 \times 10^4$	$1.11 \times 10^4$	$1.55 \times 10^3$	$6.09 \times 10^{-2}$
973	–	$7.10 \times 10^4$	$4.68 \times 10^4$	$8.15 \times 10^3$	0.85
$T/\text{K}$	$p_{\text{Mn}}^*/\text{Pa}$	$p_{\text{Cu}}^*/\text{Pa}$	$p_{\text{Fe}}^*/\text{Pa}$	$p_{\text{Zn}}^*/\text{Pa}$	$p_{\text{Pb}}^*/\text{Pa}$
1073	$2.95 \times 10^{-2}$	$1.77 \times 10^{-5}$	$7.65 \times 10^{-8}$	$3.10 \times 10^4$	7.23
1173	0.380	$4.23 \times 10^{-4}$	$2.99 \times 10^{-6}$	$9.32 \times 10^4$	$4.22 \times 10^1$
1273	3.230	$6.11 \times 10^{-3}$	$6.48 \times 10^{-5}$	–	$1.86 \times 10^2$
1373	$1.99 \times 10^1$	$6.00 \times 10^{-2}$	$8.85 \times 10^{-4}$	–	$6.55 \times 10^2$
1473	$9.47 \times 10^1$	0.40	$8.40 \times 10^{-3}$	–	$1.94 \times 10^3$

It can be seen from Table 1 that the differences of the saturation vapor pressure values of the components contained in spent dry-batteries are obvious. Because the values of  $p_{\text{Hg}}^*$  are in the range of  $3.27 \times 10^4$ – $8.88 \times 10^4$  Pa at 573–623 K and the values of  $p^*$  of Cd, Zn and  $\text{ZnCl}_2$  are  $1.89 \times 10^2$ – $7.10 \times 10^4$  Pa at 773–973 K, these four components would volatilize easily in vacuum at lower temperature ( $\leq$

973 K). Metal Mn, Cu and Fe volatilize little when the temperature is less than 1273 K because their saturation vapor pressure values are less than 3.20 Pa at 1273 K. The values of  $p_{\text{Pb}}^*$  are  $4.22 \times 10^1$ – $1.86 \times 10^2$  Pa at 1173–1273 K, where it would evaporate remarkably. Therefore, the vacuum evaporation process should be divided into two stages. The first stage is taken at 773–973 K to volatilize Hg, Cd, Zn and  $\text{ZnCl}_2$ . Then the evaporation temperature is elevated to 1173–1273 K to distill Pb, the other metal are remained in residue because of their lower vapor pressure. Pure substance or alloy is obtained by condensing the mixed gas fractionally. The recovered Hg, Cd, Zn and Pb can be reused to manufacture Zn–Mn dry-batteries.

## 2.2 Relationship between maximum evaporation rate and temperature

The production efficiency for treating spent dry-batteries in vacuum, namely the evaporation rate, is affected mainly by temperature. The evaporation rate can be described as Eqn.13<sup>[16]</sup>:

$$\omega_{\text{max}} = 2.623 \times 10^{-2} \alpha p_i^* (M/T)^{1/2} \quad (13)$$

where  $\omega_{\text{max}}$  stands for the maximum evaporation rate,  $\alpha$  is the distillation coefficient,  $M$  is molecular weight of the distilled substance. The saturation vapor pressure of the distilled substance is  $p_i^*$  when the temperature is  $T$ .

Supposing that the distillation coefficient  $\alpha = 1$ , the maximum evaporation rates of substances in spent dry-batteries were calculated at 573–1273 K according to Eqn.13 and Table 1, as listed in Table 2.

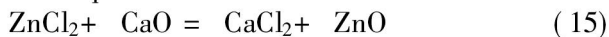
**Table 2** Relationship between maximum evaporation rate  $\omega_{\text{max}}(\text{g} \cdot \text{m}^{-2} \cdot \text{min}^{-1})$  and temperature

$T/\text{K}$	$\omega_{\text{max, Hg}}$	$\omega_{\text{max, ZnCl}_2}$	$\omega_{\text{max, Cd}}$	$\omega_{\text{max, Zn}}$
573	$5.07 \times 10^2$	$7.42 \times 10^{-3}$	$6.22 \times 10^{-2}$	$1.89 \times 10^{-3}$
623	$1.32 \times 10^3$	$1.14 \times 10^{-1}$	$3.99 \times 10^{-1}$	$1.55 \times 10^{-2}$
673	–	$7.49 \times 10^{-1}$	1.72	$9.21 \times 10^{-2}$
773	–	$1.44 \times 10^1$	$1.77 \times 10^1$	1.44
873	–	$1.30 \times 10^2$	$1.04 \times 10^2$	$1.11 \times 10^1$
973	–	$6.97 \times 10^2$	$4.17 \times 10^2$	$5.54 \times 10^1$
1073	–	–	–	$2.01 \times 10^2$
1173	–	–	–	$5.77 \times 10^2$
$T/\text{K}$	$\omega_{\text{max, Pb}}$	$\omega_{\text{max, Mn}}$	$\omega_{\text{max, Cu}}$	$\omega_{\text{max, Fe}}$
1073	$8.33 \times 10^{-2}$	$1.75 \times 10^{-4}$	$1.13 \times 10^{-7}$	$4.58 \times 10^{-10}$
1173	$4.66 \times 10^{-1}$	$2.16 \times 10^{-3}$	$2.58 \times 10^{-6}$	$1.71 \times 10^{-8}$
1273	1.97	$1.76 \times 10^{-2}$	$3.58 \times 10^{-5}$	$3.56 \times 10^{-7}$
1373	6.67	$1.04 \times 10^{-1}$	$3.38 \times 10^{-4}$	$4.68 \times 10^{-6}$
1473	$1.91 \times 10^1$	$4.80 \times 10^{-1}$	$2.21 \times 10^{-3}$	$4.29 \times 10^{-5}$

It is shown from Table 2 that the maximum evaporation rate is affected remarkably by temperature. Metal Cd, Zn and  $\text{ZnCl}_2$  are volatilized quickly at 773–973 K at maximum evaporation rates of  $1.77 \times 10^1 - 4.17 \times 10^2 \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ ,  $1.44 - 5.54 \times 10^1 \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$  and  $1.44 \times 10^1 - 6.97 \times 10^2 \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ , respectively. Because the value of  $\omega_{\max, \text{Hg}}$  is  $1.32 \times 10^3 \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$  at 623 K, metal Hg would be volatilized into vapor when Cd, Zn and  $\text{ZnCl}_2$  are evaporated. The maximum evaporation rates of Pb are  $4.66 \times 10^{-1} - 1.97 \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ ,  $10^2$  times more than that of Mn, Cu or Fe at 1 173–1 273 K, respectively. Thus, these three metals are remained in residue while Pb is concentrated in vapor in the temperature range.

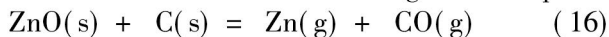
### 2.3 Behavior of $\text{ZnCl}_2$ in vacuum

It can be known from Table 1 that the value of  $p_{\text{ZnCl}_2}^*$  is  $1.29 \times 10^3 \text{ Pa}$  at 773 K. Thus,  $\text{ZnCl}_2$  volatilizes in abundance inevitably and reduces the purity of Hg, Zn and Cd. Adding CaO to the charge, however, can solve the problem and the principle based on Eqn.15



According to the thermodynamic data<sup>[18]</sup>, the value  $\Delta G_m^\circ$  of Eqn.(15) is  $-89.81 \text{ kJ/mol}$  at 800 K and  $-85.07 \text{ kJ/mol}$  at 1 000 K. Therefore, the reaction moves to the positive at a great trend in the thermodynamic view. When Hg, Zn and Cd are distilled at 773–973 K,  $\text{ZnCl}_2$  with higher vapor pressure turns into ZnO at lower vapor pressure. Thus, the influence of  $\text{ZnCl}_2$  on the purity of Hg, Zn and Cd can be eliminated. In addition, the bad effects of chlorine and gaseous sulfur can also be eliminated<sup>[19]</sup>.

Furthermore, zinc can be reduced by carbon contained in spent dry-batteries from ZnO at high temperature in vacuum. The reaction is given as Eqn.16



The Standard Gibbs free energy of Eqn.16 is expressed in Eqn.17<sup>[16]</sup>

$$\Delta G_m^\circ = 371\,204 + 43.3T \lg T - 432.33T \quad (17)$$

Supposing that  $p$  stands for the total pressure of the vacuum chamber,  $p_{\text{Zn}}$  and  $p_{\text{CO}}$  stand for the partial pressure of Zn and CO, respectively. In general,  $p_{\text{Zn}} = p_{\text{CO}}$  and  $p_{\text{Zn}} + p_{\text{CO}} = p$ . Therefore, according to Eqn.17, the Gibbs free energy of Eqn.16 can be expressed as Eqn.18

$$\begin{aligned} \Delta G &= \Delta G_m^\circ + RT \ln(p_{\text{Zn}} p_{\text{CO}}) \\ &= 371\,204 + 43.3T \lg T - 432.33T + \\ &\quad 2RT \ln(p/2) \end{aligned} \quad (18)$$

When the total pressure is  $1.013 \times 10^5 - 1.013 \text{ Pa}$ , the Gibbs free energy values of Eqn.16 were calculated at 773–1 273 K, as shown in Fig. 1.

It can be seen from Fig. 1 that the initial reaction temperature decreases with reducing the total

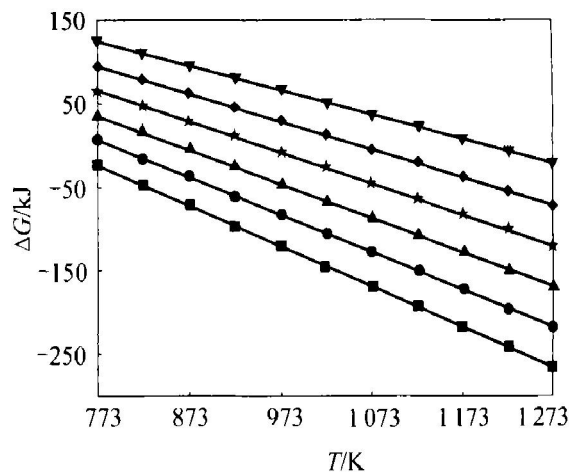


Fig. 1 Effects of temperature and pressure on Gibbs free energy of ZnO reduction

▼  $1.013 \times 10^5 \text{ Pa}$ ; ◆  $1.013 \times 10^4 \text{ Pa}$ ; ★  $1.013 \times 10^3 \text{ Pa}$ ;  
▲  $1.013 \times 10^2 \text{ Pa}$ ; ●  $1.013 \times 10^1 \text{ Pa}$ ; ■  $-1.013 \text{ Pa}$

chamber pressure in vacuum. The reaction will proceed at 787 K when the total pressure is below  $1.013 \times 10^1 \text{ Pa}$ . In order to ensure that the reduction of ZnO proceeds easily, it is necessary to keep the temperature in the range of 1 173–1 273 K and the pressure below  $1.013 \times 10^1 \text{ Pa}$ . Metal Zn is reduced into vapor and mixed with gaseous Pb. Pure Zn and Pb is further obtained by fractional condensation, respectively.

### 2.4 Behavior of $\text{MnO}_2$ in vacuum

Manganese exists as  $\text{MnO}_2$  mainly in spent dry-batteries. It can be reduced by carbon from  $\text{MnO}_2$  at an elevated temperature in vacuum described as following:



The Standard Gibbs free energy of Eqn.19 is as following Eqn. 20<sup>[18]</sup>:

$$\Delta G_m^\circ = 290\,900 - 352.37T \quad (298 - 1\,000 \text{ K}) \quad (20)$$

Supposing that  $p$  and  $p_{\text{CO}}$  stand for the total pressure of the vacuum chamber and the partial pressure of CO, respectively. In general,  $p_{\text{CO}} = p$ . Consequently, according to Eqn. 20, the Gibbs free energy of Eqn.19 can be expressed as Eqn.21:

$$\Delta G = 290\,900 - 352.37T + 2RT \ln p \quad (298 - 1\,000 \text{ K}) \quad (21)$$

When the total pressure is  $1.013 \times 10^5 - 1.013 \text{ Pa}$ , the Gibbs free energy values of Eqn.19 were calculated at 773–973 K, as shown in Fig. 2.

It can be seen from Fig. 2 that the initial reaction temperature decreases with reducing the total chamber pressure in vacuum. The reaction proceeds automatically at a great trend at 773–973 K when the total pressure is  $1.013 \times 10^1 \text{ Pa}$ . Therefore,  $\text{MnO}_2$  is reduced easily by carbon in distilling Hg, Zn and Cd at  $1.01 \times 10^1 \text{ Pa}$ . It can be also known from Table 1 and Table 2 that the value of  $p_{\text{Mn}}^*$  and  $\omega_{\max, \text{Mn}}$  at

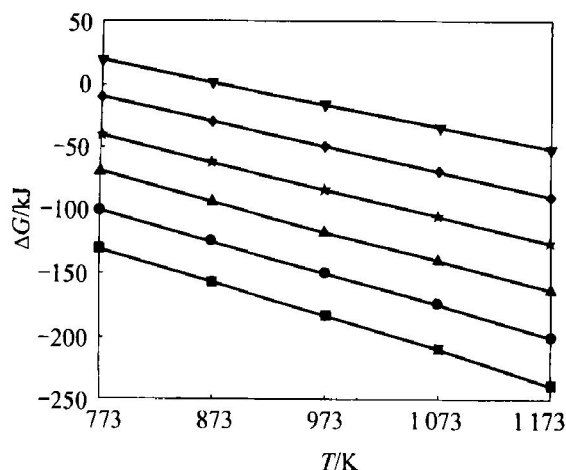


Fig. 2 Effects of temperature and pressure on Gibbs free energy of  $\text{MnO}_2$  reduction

▼— $1.013 \times 10^5$  Pa; ◆— $1.013 \times 10^4$  Pa; ★— $1.013 \times 10^3$  Pa;  
▲— $1.013 \times 10^2$  Pa; ●— $1.013 \times 10^1$  Pa; ■— $1.013$  Pa

1 273 K is  $3.23$  Pa and  $1.76 \times 10^{-2} \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ , respectively, which is about 1% as that of Pb. Thus, the reduced Mn is remained in the residue with C, Cu and Fe, if the distillation temperature does not exceed 1 273 K.  $\text{MnO}_2$  and Cu are obtained from the residual by hydrometallurgical method, which can be directly reused to manufacture zinc-manganese dry-batteries.

### 3 CONCLUSIONS

1) The valuable metals in spent dry-batteries, such as Zn, Mn, Cu, Pb, Cd and Hg, can be recycled by vacuum metallurgy in the total chamber pressure of  $1.01 \times 10^1$  Pa.

2) A fractional vacuum distillation and condensation is taken to obtain metals with high purity. Metal Hg, Cd and Zn are volatilized at 773–973 K.  $\text{MnO}_2$  and ZnO are reduced by carbon in spent dry-batteries at 773–1 273 K. Metal Pb evaporates at 1 173–1 273 K while Mn, Cu, Fe and C are remained in residue. Metal Cu and  $\text{MnO}_2$  are extracted from the residue by hydrometallurgical process.

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