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ScienceDirect
Trans. Nonferrous Met. Soc. China 21(2011) 1136−1140
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Solubility and phase diagrams of hydroxyl manganese chloride

WANG Yun-shan, ZHANG Jin-ping, YANG Gang

National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology,
Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

Received 4 June 2010; accepted 24 October 2010

Abstract: In the course of the basic research on the ammonia-evaporation reaction of manganese monoxide (MnO), hydroxyl manganese chloride ($Mn_2(OH)_3Cl$) was found. The solubility and phase diagrams of the hydroxyl manganese chloride were investigated. The aqueous thermostat and vibrating bed were used to determine the solubility of hydroxyl manganese chloride in water, ammonium chloride and manganese chloride system, and the phase diagrams of multicomponent system were drawn. The research results indicate that hydroxyl manganese chloride has been produced in laboratory and is in favor of the solid-liquid separation at high temperature.

Key words: ammonia-evaporation; hydroxyl manganese chloride; solubility; phase diagram

1 Introduction

A new integrated technological system "The acid-alkali joint production and its regeneration cycle" was developed, and extensive efforts on its basic theory and application were given out[1−4]. The new system mainly contains the decomposition of ammonium chloride into ammonia and hydrogen chloride at the presence of medium (MnO), and their regeneration cycle.

The previous research indicated that the ammonia-evaporation reaction of manganese monoxide (MnO) plays very important role in the acid-alkali joint production. The ammonia-evaporation reaction obeys reaction (1). The $Mn(OH)_2$ reacts with $MnCl_2$ to form complex hydroxyl manganese chloride ($Mn_2(OH)_3Cl$) with a neglectable solubility, following reactions (2) and (3). The formation of hydroxyl manganese chloride provides the condition of solid-liquid separation.

$$MnO+2NH_4Cl \xrightarrow{>120℃} MnCl_2+2NH_3+H_2O \tag{1}$$

$$MnO+H_2O \rightarrow Mn(OH)_2 \tag{2}$$

$$MnCl_2+3Mn(OH)_2 \rightarrow 2Mn_2(OH)_3Cl \tag{3}$$

After ammonia-evaporation reaction, the solid reactant is separated. The analytical results of the solid reactant by XRD (powder X-ray diffraction) proved the existence of $Mn_2(OH)_3Cl$. $Mn_2(OH)_3Cl$ was discovered at south Siberian altiplano in chloro-amakinite ore[5]. Usually, ammonia-evaporation reaction uses magnesium oxide (MgO) as the transforming agent[6−7]. The researches were focused on the basic property of another complex-magnesium hydroxychloride (MgOHCl)[8−10]. The basic chemical property of hydroxyl manganese chloride has not been reported yet. In this work, referring to some relative literatures[11−17], the phase diagrams of $Mn_2(OH)_3Cl-MnCl_2-NH_4Cl-H_2O$ system and the solubility of $Mn_2(OH)_3Cl$ were studied in detail.

2 Experimental

2.1 Reagent and instrument

All reagents used were analytical pure. MnO of 98% purity was got from Xiangtan of Hunan Province, China, $MnCl_2·4H_2O$ was purchased from Tianjin Chemical Regent Factory. HZS-H aqueous thermostat oscillator is made by Harbin East-union Electronic Technology Exploitation Ltd., whose precision is ±0.1 °C.

2.2 Production of $Mn_2(OH)_3Cl$

MnO and $MnCl_2$ ($MnCl_2$ is surplus 20%) were mixed on molar ratio of 3:1.2. 200 g MnO and 141.9 g $MnCl_2$ and 400 mL H_2O were put into a high pressure

Foundation item: Project (062702) supported by Innovation Funds of Institute of Process Engineering, Chinese Academy of Sciences
Corresponding author: WANG Yun-shan; Tel: +86-10-62525607; Fax: +86-10-62561822; E-mail: wangys@home.ipe.ac.cn
DOI: 10.1016/S1003-6326(11)60833-9

reactor, sealed and mixed at 120 °C for 1 h, then the mixture was discharged and hot filtered. The solid was preserved for ready-use; the concentrations of the manganese and chloride in solid phase were analyzed, and the XRD (X'Pert-Pro, the harrow material is copper) analysis was carried out after the solid sample was dried at 120 °C.

2.3 Experimental procedure

2.3.1 Determination of solubility of $Mn_2(OH)_3Cl$ in water

1.5−3.0 g $Mn_2(OH)_3Cl$ prepared was put in a pyxis containing 50 mL H_2O, then the pyxis was sealed, and three prepared pyxises were placed in an aqueous thermostat under a certain temperature, such as 25, 40, 55, 65, 80 °C. Those pyxises were vibrated for a while, then was filtered to separate solid and liquid phase. The concentration of manganese in liquid phase was analyzed in order to calculate the solubility of $Mn_2(OH)_3Cl$ in water. This step was repeated several times to make sure the system to reach a equilibrium condition).

2.3.2 Phase diagram of $Mn_2(OH)_3Cl$−NH_4Cl−H_2O

Eight samples of 1.5−3.0 g $Mn_2(OH)_3Cl$ prepared were weighed, and those eight samples were put into eight pyxises containing 50 mL NH_4Cl solution with concentrations of 30, 60, 90, 120, 150, 180, 210 and 250 g/L, respectively. Then the pyxises were sealed and placed in an aqueous thermostat under a certain temperature, were vibrated for a while, then were taken out (this step can be repeated several times to make sure the system to reach a equilibrium condition), and filtered to separate solid and liquid phase. Finally, the content of manganese in liquid was analyzed. So the phase diagram was drawn with the obtained data. The above procedure was repeated under a set of different temperature conditions.

2.3.3 Phase diagram of $Mn_2(OH)_3Cl$−$MnCl_2$−H_2O

Six samples of 1.5−3.0 g $Mn_2(OH)_3Cl$ prepared were weighed and put into six pyxises containing 50 mL $MnCl_2$ solution with concentrations of 5, 20, 35, 50, 65, 80 g/L, respectively. Those pyxises were sealed and placed in an aqueous thermostat under a certain temperature, vibrated for a while, then were taken out (also sampling and analyzing preliminary to sometime, in order to contrast whether the system has reached the equilibrium), filtered to separate solid and liquid phase. The concentration of manganese in liquid was analyzed, so the phase diagram was drawn with the obtained data. The above procedure was repeated under a set of different temperature conditions.

2.3.4 Phase diagram of $Mn_2(OH)_3Cl$−NH_4Cl−$MnCl_2$−H_2O system

Nine samples of 1.5−3.0 g $Mn_2(OH)_3Cl$ prepared were weighed and placed into pyxises containing 50 mL NH_4Cl and $MnCl_2$ solution with concentrations of 250 and 0, 220 and 10, 190 and 20, 160 and 30, 130 and 40, 100 and 50, 70 and 60, 40 and 70, 0 and 80 g/L, respectively. Those pyxises were sealed and placed in an aqueous thermostat under a certain temperature, vibrated for a while taken out, filtered to separate solid and liquid, and the concentration of manganese in liquid was analyzed, and the phase diagram was drawn with the obtained data. The above procedure was respeated under a set of different temperature conditions.

2.4 Analytical methods

The concentrations of manganese in samples were determined by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectra, PE DV5300), and the content of Cl^- was analyzed by mercurimetry.

3 Results and discussion

3.1 Analysis of $Mn_2(OH)_3Cl$

The lab-made $Mn_2(OH)_3Cl$ was prepared and then analyzed by the method mentioned. The experimentally determined molar ratio of manganese to chloride in the $Mn_2(OH)_3Cl$ is 2.05, which coincides with the theoretical value of $Mn_2(OH)_3Cl$. The XRD pattern of the lab-made $Mn_2(OH)_3Cl$ is shown in Fig.1.

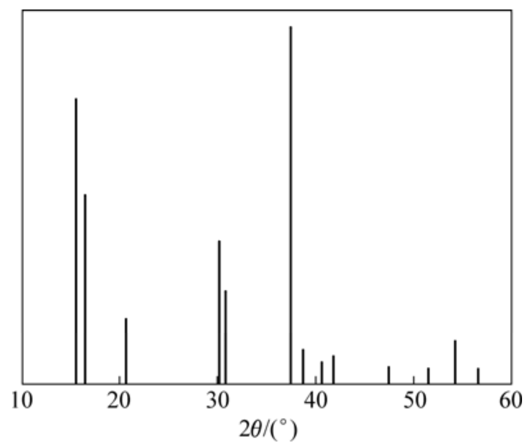

Fig.1 XRD pattern of lab-made $Mn_2(OH)_3Cl$

Comparison of the measured pattern with the standard one of $Mn_2(OH)_3Cl$ in XRD analytical database shows that the prepared substance is hydroxyl manganese chloride.

3.2 Solubility of $Mn_2(OH)_3Cl$ in water

The solubility of $Mn_2(OH)_3Cl$ in water under different temperatures was obtained, and is shown in Fig.2.

The experimental results indicate that the solubility of $Mn_2(OH)_3Cl$ in water is very small, and it is between microsolubility substance and infusibility substance.

Using this property of $Mn_2(OH)_3Cl$, the separation of manganese chloride and ammonium chloride can be realized at high temperature.

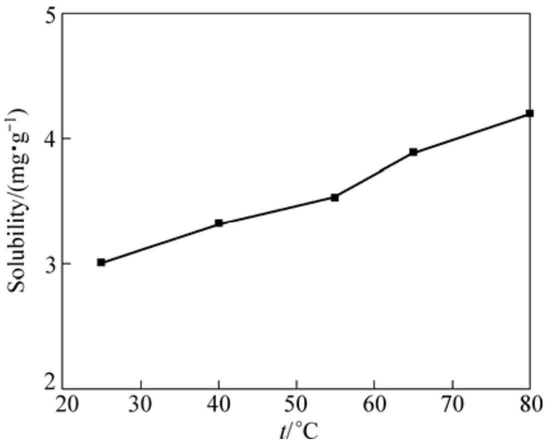

Fig.2 Solubility of $Mn_2(OH)_3Cl$ in water

3.3 Solubility of $Mn_2(OH)_3Cl$ in $Mn_2(OH)_3Cl$−NH_4Cl−H_2O system

The solubilities of $Mn_2(OH)_3Cl$ in the $Mn_2(OH)_3Cl$−NH_4Cl−H_2O system under different temperatures are shown in Fig.3.

The experimental results indicate that the solubility of $Mn_2(OH)_3Cl$ increases with the increase of concentration of NH_4Cl in the $Mn_2(OH)_3Cl$−NH_4Cl−H_2O system under a constant temperature. When NH_4Cl in the system decomposes continually, its concentration decreases, resulting in the decrease of solubility and precipitation of $Mn_2(OH)_3Cl$. This is favorable to the transformation of $MnCl_2$ to $Mn_2(OH)_3Cl$ (Reaction (3)). Moreover, when NH_4Cl concentration in the system keeps constant, the solubility of $Mn_2(OH)_3Cl$ slightly increases with the increase of temperature, but the increasing amplitude is small. When the concentration of NH_4Cl is low, the variation of the solubility of $Mn_2(OH)_3Cl$ is negligible at different temperatures. This

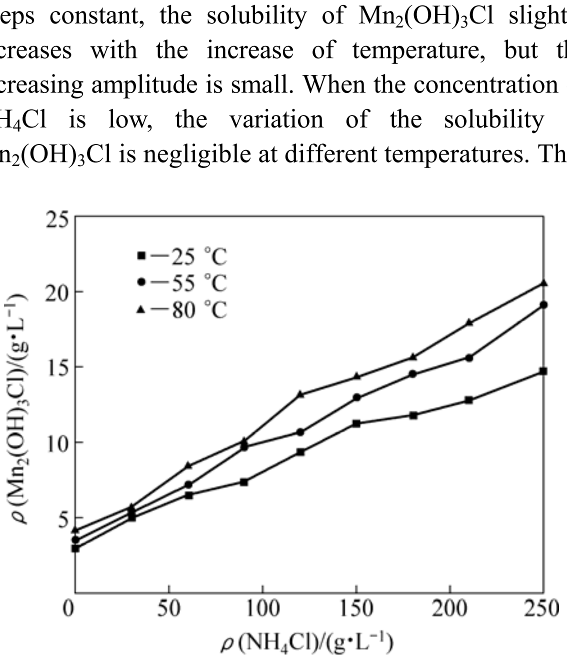

Fig.3 Solubility values of $Mn_2(OH)_3Cl$ in $Mn_2(OH)_3Cl$−NH_4Cl−H_2O system at different temperatures

result indicates the separation feasibility of NH_4Cl and $MnCl_2$ in the slurry after ammonia-evaporation reaction of MnO at high temperature.

3.4 Solubility of $Mn_2(OH)_3Cl$ in $Mn_2(OH)_3Cl$−$MnCl_2$−H_2O system

The solubility data of $Mn_2(OH)_3Cl$ in the $Mn_2(OH)_3Cl$−$MnCl_2$−H_2O system at different temperatures are shown in Fig.4.

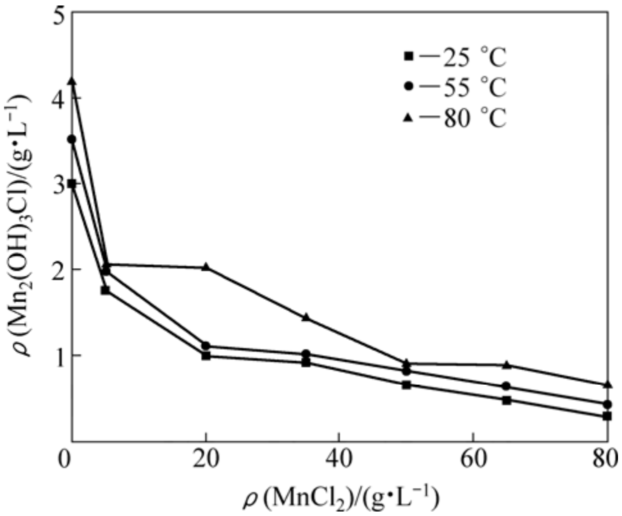

Fig.4 Solubility values of $Mn_2(OH)_3Cl$ in $Mn_2(OH)_3Cl$−$MnCl_2$−H_2O system at different temperatures

The experimental results indicate that the solubility of $Mn_2(OH)_3Cl$ decreases gradually with the increase of $MnCl_2$ concentration in the $Mn_2(OH)_3Cl$−$MnCl_2$−H_2O system at a constant temperature, and the solubility is very small because $MnCl_2$ has strong salting-out action on $Mn_2(OH)_3Cl$. This result is in favor of the reaction course of the ammonia-evaporation of MnO. Along with the proceeding of the reaction, $MnCl_2$ continuously transforms into $Mn_2(OH)_3Cl$, so the $MnCl_2$ concentration in the reaction system keeps at low level (<100 g/L) and the reaction proceeds forward. Moreover, when $MnCl_2$ concentration in the reaction system keeps constant, the solubility of $Mn_2(OH)_3Cl$ has a little increment with the increase of temperature, but the increasing amplitude is small. The result provides a evidence to realize solid-liquid separation of the slurry of ammonia-evaporation reaction of MnO at higher temperature.

3.5 Solubility of $Mn_2(OH)_3Cl$ in $Mn_2(OH)_3Cl$−NH_4Cl−$MnCl_2$−H_2O system

The solubility data of $Mn_2(OH)_3Cl$ in the $Mn_2(OH)_3Cl$−NH_4Cl−$MnCl_2$−H_2O system at different temperatures are shown in Figs.5−7.

The experimental results indicate that, firstly, the change of NH_4Cl concentration is the major factor to influence the change of $Mn_2(OH)_3Cl$ concentration in the

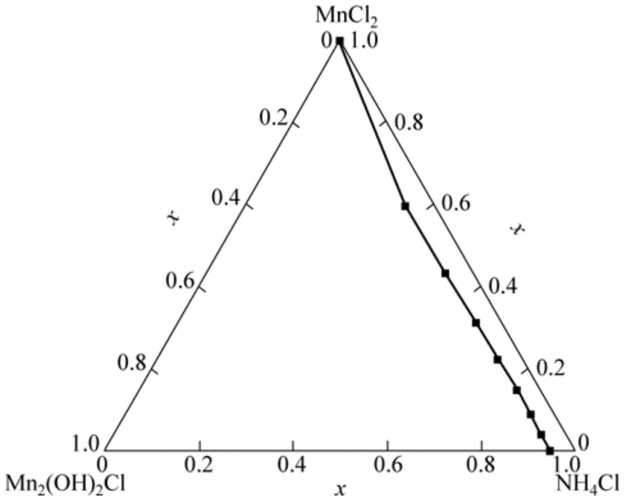

Fig.5 Solubility of $Mn_2(OH)_3Cl$ in $Mn_2(OH)_3Cl$−NH_4Cl−$MnCl_2$−H_2O system at 25 °C

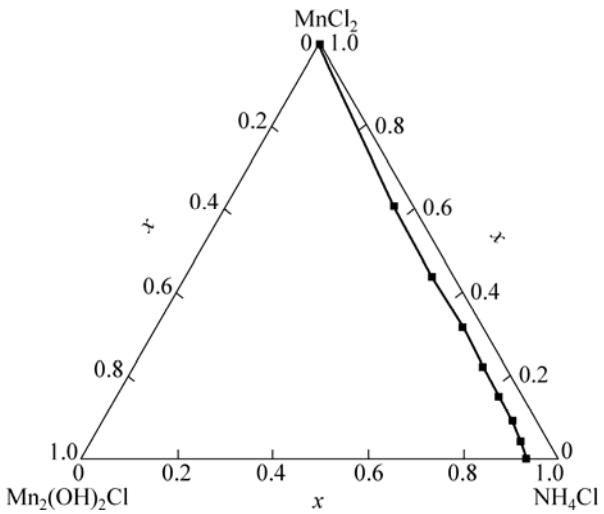

Fig.6 Solubility of $Mn_2(OH)_3Cl$ in $Mn_2(OH)_3Cl$−NH_4Cl−$MnCl_2$−H_2O system at 55 °C

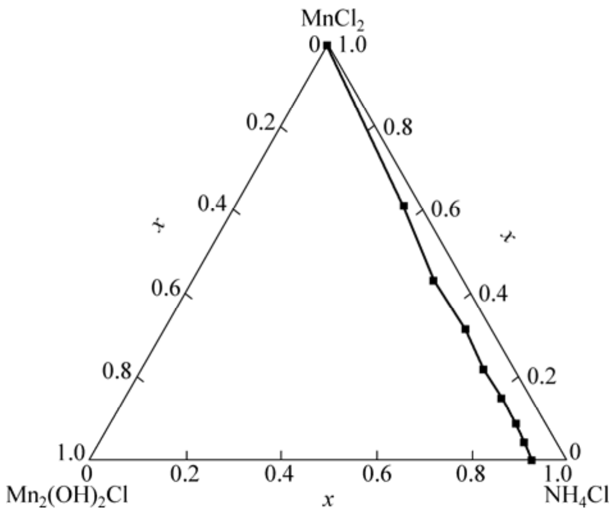

Fig.7 Solubility of $Mn_2(OH)_3Cl$ in $Mn_2(OH)_3Cl$−NH_4Cl−$MnCl_2$−H_2O system at 80 °C

$Mn_2(OH)_3Cl$−NH_4Cl−$MnCl_2$−H_2O system. The higher the concentration of NH_4Cl is, the larger the solubility of $Mn_2(OH)_3Cl$. Whereas, when the NH_4Cl continuously decomposes to form ammonia and emits from the system, the concentration of NH_4Cl decreases, resulting in the decrease of the solubility of $Mn_2(OH)_3Cl$. The results are in agreement with the analytical results mentioned in section 3.3. Secondly, the phase diagram of quaternary system indicates that the influence of the change of the $MnCl_2$ concentration on the change of the $Mn_2(OH)_3Cl$ concentration is negligible, and the results are in agreement with the analytical results mentioned in sections 3.3 and 3.4, respectively. Thirdly, the influence of temperature on the quaternary system is the same as it on the ternary system. This result proves that the solid-liquid separation of the $Mn_2(OH)_3Cl$−NH_4Cl−$MnCl_2$−H_2O system at high temperature is feasible.

4 Conclusions

1) $Mn_2(OH)_3Cl$ is prepared successfully. The experimental data of the solubility and the ternary system and quaternary system phase diagrams of $Mn_2(OH)_3Cl$ indicate that $Mn_2(OH)_3Cl$ has microsolubility; the influence of the concentration of NH_4Cl on its solubility is large, and the influence of temperature and the concentration of $MnCl_2$ on its solubility is slight.

2) The solubility of $Mn_2(OH)_3Cl$ and the ternary system and quaternary system phase diagrams of ammonia-evaporation system offer the evidence for the solid-liquid separation at high temperature.

References

[1] YANG Gang. Principle and technology of producing hydrochloric acid “in new process of molten hydrolysis of alkali chloride joint production of hydrochloric acid and alkali carbonate” [D]. Beijing: Institute of Process Engineering, Chinese Academy of Sciences, 2006: 1−3. (in Chinese)

[2] ZHANG Jin-ping. Fundamental research of “joint production acid-base and regeneration cycle”-technology and principle of producing alkali [D]. Beijing: Institute of Process Engineering, Chinese Academy of Sciences, 2008: 1−3. (in Chinese)

[3] WANG Yun-shan. Study on the new method and technology of comprehensive utilization of seabed manganese nodules [D]. Beijing: Institute of Process Engineering, Chinese Academy of Sciences, 2006: 87−88. (in Chinese)

[4] SUN Yong. The application of process of the “acid-alkali joint production and regeneration” to the high-value conversion of corn straw [D]. Beijing: Institute of Process Engineering, Chinese Academy of Sciences, 2007: 13−15. (in Chinese)

[5] BERNHARDT S E, NIKOLAI S R, ALEXANDER G P. Evidence for hibbingtie-kempite solid solution [J]. Mineralogical Magazine, 1998, 62(2): 251−255.

[6] CHRISTENSEN N C. Recovery and decomposition of $MgCl_2$: United States, 2413292 [P]. 1946−12−31.

[7] KIPOUROS G J, SADOWAY D R. A thermochemical analysis of the production of anhydrous $MgCl_2$ [J]. Journal of Light Metals, 2001,

1(2): 111−117.
[8] KASHANI-NEJAD S, NG K W, HARRIS R. Preparation of MgOHCl by controlled dehydration of $MgCl_2·6H_2O$ [J]. Metallurgical and Materials Transactions B, 2004, 35(2): 405−406.
[9] KASHANI-NEJAD S, NG K W, HARRIS R. Properties of MgOHCl [J]. Metallurgical and Materials Transactions B, 2004, 35(2): 406−408.
[10] KASHANI-NEJAD S, NG K W, HARRIS R. MgOHCl thermal decomposition kinetics [J]. Metallurgical and Materials Transactions B, 2005, 36(1): 153−157.
[11] NIU Zi-de, CHENG Fang-qin. Water-salt system phase diagrams and its application [M]. Tianjin: Tianjin University Press, 2002. (in Chinese)
[12] ATHBIR A, HADEK M E, COHEN-ADAD R. Solid-liquid equilibria in the quaternary system $NaCl-FeCl_2-FeCl_3-H_2O$ [J]. Fluid Phase Equilibria, 2001, 181(1−2): 187−194.
[13] TRYPUĆ M, KIELKOWSKA U. Phase diagram for the system $KVO_3+NH_4HCO_3+NH_4VO_3+KHCO_3+H_2O$ at 303 K [J]. Fluid Phase Equilibria, 2005, 230(1−2): 99−104.
[14] LIN B, MCCORMICK A V, TED DAVIS H, STREY R. Solubility of sodium soap in aqueous salt solutions [J]. Journal of Colloid and Interface Science, 2005, 291(2): 543−549.
[15] DAGADE D H, KUMBHAR R R, SABALE S R, PATIL K J. Phase diagram of $Na_2S_2O_3$+ethanol+water at ambient pressure and temperature [J]. Fluid Phase Equilibria, 2007, 255(2): 110−114.
[16] WANG Chong-lin. Phase diagrams theory and its application[M]. Beijing: Higher Education Press, 2008. (in Chinese)
[17] DENG Tian-long, LI Dong-chan. Solid-liquid metastable equilibria in the quaternary system ($NaCl-KCl-CaCl_2-H_2O$) at 288.15 K [J]. Fluid Phase Equilibria, 2008, 269(1−2): 98−103.

羟基氯化锰的溶解度及相图性质

王云山，张金平，杨 刚

中国科学院 过程工程研究所 湿法冶金清洁生产技术国家工程实验室，北京 100190

摘 要：在进行氧化亚锰(MnO)蒸氨反应的基础研究过程中，发现羟基氯化锰($Mn_2(OH)_3Cl$)这一物质。对该羟基氯化锰的溶解度和相图等进行系统研究；利用恒温水浴和摇床测定不同温度下羟基氯化锰在水中、氯化铵中及氯化锰等体系中的溶解度，并绘制其在多元体系中的相图。实验制备了该物质，并得出羟基氯化锰有利于蒸氨反应中高温固液分离的结论。

关键词：蒸氨；羟基氯化锰；溶解度；相图

(Edited by YANG Hua)