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Water balance analysis and wastewater recycling investigation in electrolytic manganese industry of China — A case study

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ABSTRACT

A water balance investigation was performed for a representative electrolytic manganese metal (EMM) enterprise to study the details of water consumption and generation in the production process. A new integrated wastewater treatment approach was put forward to recover useful chemicals from the process wastewater, which contained high concentrations of Mn^{2+}, Cr(VI), Cr^{3+}, and NH_4^+. Cr(VI) was recovered from the wastewater by ion exchange techniques and reused as EMM passivant. The remaining wastewater containing Mn^{2+} and NH_4^+ was returned to the leaching section before the impurity removal procedure to prepare electrolytes. Complete wastewater recycling was achieved after water balance regulation and optimization. Final demonstration line results proved that the proposed process is feasible and exhibits significant advantages of better treatment effects, lower costs and lower environmental impact compared to the traditional reduction–neutralization–sedimentation treatment method. With the adoption of the proposed approach, solid waste disposal cost and the required area for the landfill yard were decreased by 80%. Operating costs for wastewater treatment were lowered by 85%. Around 4.8 kg/t EMM of Mn^{2+}, 5.2 kg/t EMM of NH_4^+ and 0.24 kg/t EMM of Cr(VI) were recovered. The recycled wastewater proportion was increased from 6.2% to 100.0%. 1.168 m^3/t EMM of fresh water was saved and the equivalent amount of discharging wastewater was reduced to the environment.

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1. Introduction

Metallic manganese is an important alloy element (Hagelstein, 2009), which is widely used to prepare stainless steels (Zhu and Zhang, 1997) and other alloys with Ni (Kelly et al., 2003; Yang et al., 2004), Zn (Díaz-Arista et al., 2009), Te (Galvanauskaite et al., 2011; Sharma et al., 2004) and Sn (Gong and Zangari, 2003). It is mainly produced by electrolysis method (Sulcius et al., 2013; Sun et al., 2011). Since the first EMM production plant was founded in 1956, the Chinese EMM industry has developed at a fast rate. China has become the largest EMM producing country, accounting for over 98% of the world's overall EMM production capability and output.

Fig. 1 summarizes detailed data of China's EMM industry in the past 13 years. It can be seen that the capacity and output increased year by year until 2012. Compared with the capacity and output in 2000, corresponding values in 2011 were increased 16.1 and 11.0 fold respectively. However, adverse factors including increased production costs, export tax implementation, and global demand depression all led to the reduced EMM demand and increased production overcapacity. The capacity and output were found to decrease for the first time in 2012. The good news is that export tax has been canceled since January 2013, which can stimulate the market to a certain extent and is helpful for the EMM industry (Liu et al., 2007; Tan, 2013; Tan and Mei, 2005).

With the increasing development of the EMM industry, water pollution has been a serious problem and a great challenge for the EMM enterprises. It is reported that, to produce 1 t of EMM, approximately 1–3 t of wastewater is discharged into the environment (Duan et al., 2010). The average annual wastewater amount in the past 13 years was estimated to be 1.55 million t. High concentrations of Mn^{2+} (2000 mg/L), Cr(VI) (300 mg/L), and NH_3–N (2800 mg/L) ions (before treatment) were contained in the wastewater (Duan et al., 2011). It's well known that Cr(VI) is extremely carcinogenic and toxic. Cr(VI) may cause death to animals and humans (Zayed and Terry, 2003) while Cr^{3+} is somewhat less toxic and even essential for mammals (Pantsar-Kallio and Manninen, 1997; Serkan and Mustafa, 2011). Excessive Mn accumulation in human bodies can lead to brain and respiratory tract damage. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson's disease, lung embolism and bronchitis. When men are exposed to manganese for a longer period of time they may become

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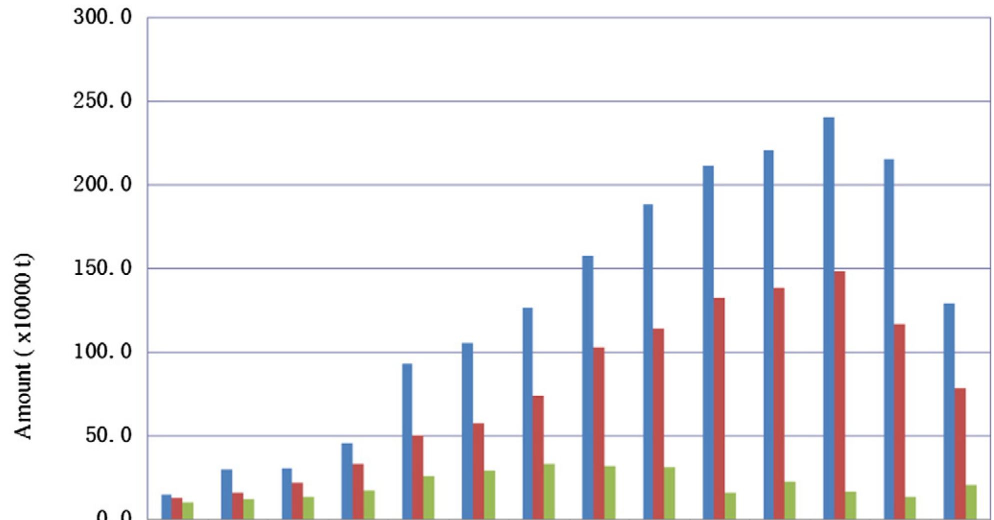

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	Aver
capacity	14.0	29.0	30.0	45.0	92.6	104.9	125.8	157.0	187.9	211.0	220.0	240.0	215.0	128.6
output	12.3	15.2	21.2	32.5	49.4	56.6	73.3	102.4	113.9	131.7	137.6	148.0	116.0	77.7
exportation	9.3	11.6	12.7	16.5	25.5	28.4	32.3	31.2	30.5	15.5	22.2	16.2	13.0	20.4

Fig. 1. Chinese EMM production capacity, output, and exportation from 2000 to 2012.

impotent. A syndrome that is caused by manganese has symptoms such as schizophrenia, dullness, weak muscles, headaches and insomnia (Lee et al., 2009; Tobiason et al., 2008). Ammonia nitrogen contributes to accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water (Huang et al., 2010).

Traditionally, the wastewater is treated by the end-of-pipe processes of reduction–neutralization–sedimentation with ferrous sulfate (or scrap iron) and lime slurry (Fig. 2) (Duan et al., 2010), so that Cr(VI) was reduced to Cr^{3+} and then co-precipitated with Mn^{2+} to form residues that need to be disposed. Due to the larger solubility product of $Mn(OH)_2$ (2.0×10^{-13}) (Liu et al., 2011), the wastewater pH must be controlled above 9.67 to make sure that Mn^{2+} can be thermodynamically deposited and its effluent concentration decreases below 2 mg/L, which is the level II standard of the "Integrated Wastewater Discharge Standard of China" (GB 8978-1996). Large amounts of alkali were required to fully deposit Mn^{2+}, leading to higher operating cost. Besides, Mn and Cr were both discharged as solid waste, leading to severe resource waste and amounts of dangerous solid residues generated. It should also be pointed out that the NH_4^+-containing wastewater after removal of Cr and Mn was always directly discharged without any further treatment due to higher treatment cost and poor treating efficiency for most EMM enterprises. All those generated solid waste and wastewater greatly polluted the surrounding environment, and led to crisis for human being's health and ecological environment (Table 1).

Currently, due to the frequent pollution incidents, the Chinese government has taken some important measures to effectively control and treat the current pollution such as increasing the management and supervision, application of stricter discharge standards and operating protocols as well as closure of non-conforming operations of the pollutant emission status for all the related enterprises. Severe financial punishment and strict suspending operations for rectifying and improving have been carried out to solve the pollution. As the stricter policy published, most of the EMM production enterprises can't meet the requirement. Extra funds were invested to further deal with the wastewater, being a heavy burden for enterprises and hindering their development. To improve the current situation, the traditional wastewater treatment process must be changed. More challenging work is needed to be done especially in reducing water consumption, controlling the process and recovering chemicals and manganese from the discharged wastewater. New methods and technology were required urgently. To

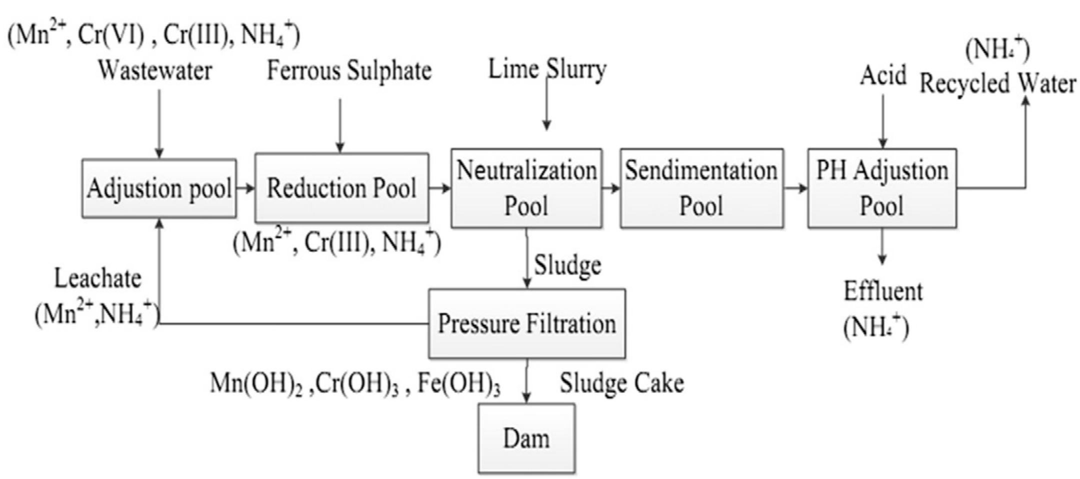

Fig. 2. Wastewater treatment process in the EMM production process.

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