

# **AMMONIUM REMOVAL FROM LANDFILL LEACHATE**

## **BY CHEMICAL PRECIPITATION**

X. Z. LI<sup>1\*</sup>, Q. L. ZHAO<sup>2</sup> and X. D. HAO<sup>3</sup>

<sup>1</sup>Department of Civil & Structural Engineering, The Hong Kong Polytechnic University,  
Hung Hom, Kowloon, Hong Kong

<sup>2</sup>School of Municipal & Environmental Engineering, Harbin University of Civil Engineering &  
Architecture, 202 Haihe Road, Nangang District, Harbin 15001, P.R. of China

<sup>3</sup>The Research Center of Ecological Economics and Environmental Technology, Shanxi  
University of Finance and Economics, 696 Wucheng Road, Taiyuan, Shanxi 030006, P. R. of  
China

---

\* Author to whom all correspondence should be addressed (Tel: +852 2766 6016; Fax: +852 2334 6389; E-mail:  
cexzli@polyu.edu.hk).

**Abstract** — the landfill leachate in Hong Kong usually contains quite high  $\text{NH}_4^+$ -N concentration, which is well known to inhibit nitrification in biological treatment processes. A common pre-treatment for reducing high strength of ammonium ( $\text{NH}_4^+$ -N) is by an air-stripping process. However, there are some operational problems such as carbonate scaling in the process of stripping. For this reason, some technical alternatives for  $\text{NH}_4^+$ -N removal from leachate need to be studied. In this study, a bench-scale experiment was initiated to investigate the feasibility of selectively precipitating  $\text{NH}_4^+$ -N in the leachate collected from a local landfill in Hong Kong as magnesium ammonium phosphate (MAP). In the experiment, three combinations of chemicals,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{MgO} + 85\% \text{ H}_3\text{PO}_4$ , and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , were used with the different stoichiometric ratios to generate the MAP precipitate effectively. The results indicated that  $\text{NH}_4^+$ -N contained in the leachate could be quickly reduced from 5,618 mg/l to 112 mg/l within 15 minutes, when  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  were applied with a  $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$  mole ratio of 1:1:1. The pH range of the minimum MAP solubility was discovered to be between 8.5 and 9.0. Attention should be given to the high salinity formed in the treated leachate by using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , which may affect microbial activity in the following biological treatment processes. The other two combinations of chemicals [ $\text{MgO} + 85\% \text{ H}_3\text{PO}_4$  and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ] could minimise salinity after precipitation, but they were less efficient for  $\text{NH}_4^+$ -N removal, compared with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . COD had no significant reduction during this precipitation. It was found that the sludge of MAP generated was easily settled within 10 minutes to reach its solids content up to 27%. The other characteristics including capillary suction time (CST) and dry density (DD) of the MAP sludge were also tested. The experimental results indicate that the settled sludge is quite solid and can be directly dumped at a landfill site even without any further dewatering treatment.

*Key words*— ammonium ( $\text{NH}_4^+$ -N); landfill leachate; precipitation; magnesium-ammonium-phosphate (MAP).

## **INTRODUCTION**

One of the major environmental concerns associated with landfilling of municipal solid wastes is related to the discharge of leachate into the environment, which may cause serious pollution to groundwater aquifers as well as adjacent surface waters<sup>1</sup> (Shultz and Kjeldsen, 1986). Leachates generated owing to moisture release, precipitation and infiltration, are easily increased by soluble or suspended organic matters, ammonium-nitrogen and inorganic ions such as heavy metals, and may cause severe environmental hazards if they are not properly collected, treated and safely disposed.

In Hong Kong, there are 13 municipal landfills; the high strengths of ammonium ( $\text{NH}_4^+ \text{-N}$ ) are a common feature of the local leachates generated at these landfills. Normally, those leachates generated at the domestic waste landfills such as the WENT landfill<sup>2</sup> (EPD, 1996) contain 3,000 to 6,000 mg/l of  $\text{NH}_4^+ \text{-N}$ ; the leachates generated at the mixed sites receiving both construction waste and domestic wastes may contain less  $\text{NH}_4^+ \text{-N}$  in the range of 1,000 to 2,500 mg/l.

The leachates generated in the Hong Kong landfills have also a second common feature: the low ratios of  $\text{BOD}_5/\text{COD}$  and  $\text{COD}/\text{NH}_4^+ \text{-N}$ . For example, the leachate generated at the WENT landfill contains not only a high concentration of  $\text{NH}_4^+ \text{-N}$  (over 5,000 mg/l), but also a high concentration of refractory organic matter with a soluble COD concentration of 6,000 to 7,000 mg/l and a  $\text{BOD}_5$  concentration of 1,500 mg/l. The features of this leachate are caused by domestic waste and also by long-term storage.

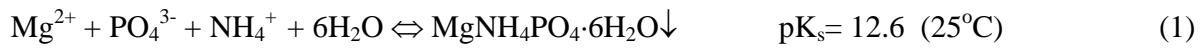
Leachates with such high NH<sub>4</sub><sup>+</sup>-N content are generally difficult of access to conventional biological treatment processes. A previous study (Li and Zhao, 1998)<sup>3</sup> confirmed that the performance of a conventional activated sludge process could be significantly affected by a high concentration of NH<sub>4</sub><sup>+</sup>-N. The COD removal declined from 95.1% to 79.1%, and the dehydrogenase activity of activated sludge decreased from 11.04 to 4.22 µg TF/mg MLSS, respectively, when the NH<sub>4</sub><sup>+</sup>-N concentration in wastewater increased from 50 to 800 mg/l. Under certain conditions, the leachates with a high concentration of NH<sub>4</sub><sup>+</sup>-N can be biologically treated, but a large amount of effluent needs to be recycled to the aeration tank so as to dilute the ammonia toxicity to a low level. This type of biological process with a high ratio of effluent recirculation causes a much higher operation cost and also occupies a much larger aeration tank than a conventional biological process does. Therefore, it might not be the best technical solution in Hong Kong.

Nowadays, the most common method for eliminating a high concentration of NH<sub>4</sub><sup>+</sup>-N (>3,000 mg/l) involved in wastewater treatment technologies is the air stripping process. But a major concern about ammonia air stripping is the release of NH<sub>3</sub> into the atmosphere so as to cause severe air pollution if ammonia can not be properly absorbed with either H<sub>2</sub>SO<sub>4</sub> or HCl. The other concern is calcium carbonate scaling of the stripping tower, when lime is used for pH adjustment. Since the leachate from an aged landfill contains a high alkalinity just like a strong pH buffering system, the pH variation before and after stripping will consume a large amount of alkali (20 g/l of caustic soda is required to increase pH) and acid (10 ml/l of chloric acid is required to absorb NH<sub>3</sub> stripped out). A huge amount of carbonate precipitate is usually formed in the process and

may cause severe operation and maintenance problems. Moreover, a large stripping tower will be needed due to foaming when  $\text{NH}_4^+$ -N in raw leachate is stripped out.

For the above reasons, other technically effective alternatives to eliminate  $\text{NH}_4^+$ -N in leachates need to be ascertained. The precipitation of  $\text{NH}_4^+$ -N by forming magnesium ammonium phosphate (MAP) precipitate has been studied and practised for different types of wastewater, such as tannery effluent in leather industries<sup>4</sup> (Tünay *et al.*, 1997), digester supernatant<sup>5, 6</sup> (Siegrist *et al.*, 1994; Siegrist, 1996) in wastewater treatment plants, wastewater from coke plants and nitrogen works<sup>7</sup> (Zdybiewska and Kula, 1991) and also sludge liquor<sup>8</sup> (Schulze-Rettmer, 1991). These studied results indicated very efficient removals of  $\text{NH}_4^+$ -N. Cost estimates indicated that the cost of precipitation process is roughly similar to the cost of nitrification and denitrification of 1 m<sup>3</sup> communal wastewater<sup>8</sup> (Schulze-Rettmer, 1991), and similar to or about 20% more expensive than that of air stripping<sup>5</sup> (Siegrist *et al.*, 1994).

Chemical precipitation as MAP can form virtually or completely insoluble compounds that can be easily separated from the water phase. For example, its insoluble form of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  with a low solubility of 0.023 g/100 ml-H<sub>2</sub>O at 0°C is well known in analytical chemistry. This product is also mineralogically known as struvite found in guano. The reaction is expressed below:

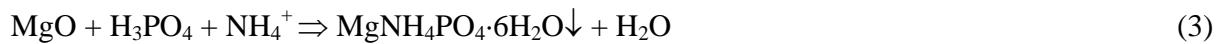


Since the mole weight of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  is 245 g/mol, 17.5 g  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  should be theoretically formed as precipitated sludge, when 1 g of  $\text{NH}_4^+$ -N is removed. Because MAP has a similar composition of Mg, P and N to that of commercial fertilisers in soil, this product could have potential to be utilised as an additive to compost, garden soil or dried sewage sludge<sup>6</sup> (Siegrist, 1996). Besides, it can also possibly be used as a fire retardant in fabrics<sup>9</sup> (Perry and Philips, 1995).

The removal of  $\text{NH}_4^+$ -N from landfill leachate by MAP precipitation was studied by Base *et al.*, 1997 in Korea, but the concerned concentration of  $\text{NH}_4^+$ -N was not very high, just in the range of 1,400 to 1,800 mg/l. This study was aimed to study the removal of as high as over 5,000 mg/l of  $\text{NH}_4^+$ -N concentration contained in leachates by precipitating it as MAP. As a typical leachate with the high concentration of  $\text{NH}_4^+$ -N was generated at the WENT landfill, it was thus taken for the study. The leachate represented the typical composition of the leachate from an aged methanogenic landfill<sup>11</sup> (Henry *et al.*, 1987) with high conductivity and alkalinity, a low  $\text{BOD}_5/\text{COD}$  ratio of 0.2 and a low COD / $\text{NH}_4^+$ -N of 1.5.

## BASIC CHEMICAL REACTIONS

The basic chemical reaction to form MAP has been expressed in Equation (1). The theoretical amounts of chemicals needed to precipitate  $\text{NH}_4^+$ -N can be calculated from following equations:



To remove all  $\text{NH}_4^+$ -N (5,618/5,325 mg/l) contained in the 500-ml leachate, the stoichiometric amounts of chemicals are either 40.73/38.61 g of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 71.83/68.08 g of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , or 8.03/7.61 g of  $\text{MgO}$  and 23.15/21.94 g (equivalent to 13.54/12.83 ml) of 85%  $\text{H}_3\text{PO}_4$ , or 19.66/18.64 g of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  and 38.46/36.45 g of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , when the  $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$  mole ratio of 1:1:1 is employed. From these calculations, the other stoichiometric amounts at the different  $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$  mole ratios can be easily obtained, as listed in Table 1.

[Table 1]

## METHODS

The raw leachate was collected from the WENT landfill and stored in a cool room prior to the experiment. The basic characteristics of the leachate are summarised in Table 2. Two leachate samples collected for the study have  $\text{NH}_4^+$ -N concentrations of 5,618 and 5,325 mg/l respectively.

[Table 2]

The MAP precipitating tests were carried out in 500-ml beakers as a batch mode. The experimental procedures were outlined below:

- 1) to weigh chemicals (see Table 1) and to measure the 500-ml raw leachate for each test;

- 2) to put the measured leachate samples and the weighed chemicals into beakers;
- 3) to start magnetic stirrers at the bottom of beaker and to monitor pH of the samples;
- 4) to react for 15 minutes until a stable pH indicated (equilibrium state);
- 5) to stop magnetic stirrers and to settle for 15 minutes;
- 6) to adjust pH for the minimum MAP solubility with 10 M NaOH solution;
- 7) to collect the supernatant above the MAP precipitate to measure the required parameters;
- 8) to use mixed liquor and the generated MAP sludge to examine its characteristics.

The three combinations of chemicals,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{MgO} + 85\% \text{ H}_3\text{PO}_4$ , and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , were respectively tested. Totally 13 sets of the  $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$  ratios were applied (11 sets for  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ; the other two for  $\text{MgO} + 85\% \text{ H}_3\text{PO}_4$  and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), as listed in Table 1.

When the optimal  $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$  ratio by using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  was determined, the additional batch tests with the same leachate were undertaken to investigate the effect of pH on the remaining  $\text{NH}_4^+ \text{-N}$ . After reaction and sludge sedimentation, the supernatant was separated from the settled MAP sludge and 10 M NaOH solution was progressively added into the supernatant to explore the minimum solubility of MAP sludge. The pH and remaining  $\text{NH}_4^+ \text{-N}$  were carefully monitored during the addition of NaOH.

In the analyses, both the raw leachate and the supernatant were measured for the parameters of pH,  $\text{NH}_4^+ \text{-N}$ , conductivity, total dissolved solids (TDS), fixed dissolved solids (FDS), and total and soluble COD. The sludge characteristics were evaluated with settled sludge volume (SSV), capillary suction time (CST), solids content (SD) and dry density (DD). pH and  $\text{NH}_4^+ \text{-N}$  were

measured with an expandable ion analyser (EA940, Orion Research Incorporation); conductivity was measured with a YSI model 33 S-C-T meter; the other parameters such as COD, TDS, FDS, SSV, CST, SC and DD were measured by the Standard Methods<sup>12</sup> (APHA, 1985).

## RESULTS AND DISCUSSION

### MAP precipitation

#### *Basic batch tests with $MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$*

The leachate samples containing the  $NH_4^+$ -N concentration of 5,618 mg/l were tested by adding  $MgCl_2 \cdot 6H_2O$  and  $Na_2HPO_4 \cdot 12H_2O$  and the precipitation results are illustrated in Fig. 1 and 2. It was found that after adding  $MgCl_2 \cdot 6H_2O$  and  $Na_2HPO_4 \cdot 12H_2O$  into the leachate samples, white colour precipitant was rapidly formed and it quickly settled at the bottom of beakers after stirring was stopped. The analytical results of supernatant demonstrated that  $NH_4^+$ -N was efficiently decreased from an initial concentration of 5,618 mg/l to as low as 210 mg/l at the  $Mg^{2+}:NH_4^+:PO_4^{3-}$  mole ratio of 1:1:1. Overdosing either  $Mg^{2+}$  or  $PO_4^{3-}$  about 10% further lowered the remaining  $NH_4^+$ -N concentration to 112 mg/l or 158 mg/l, respectively; any further over-dosages of  $Mg^{2+}$  or  $PO_4^{3-}$  did not achieve additional  $NH_4^+$ -N removal. From an engineering point of view, it may be practical to control the  $Mg^{2+}:NH_4^+:PO_4^{3-}$  mole ratio at 1:1:1 when the leachate needs to precipitate  $NH_4^+$ -N as MAP, as expressed theoretically in Equation (2).

[Fig. 1]

[Fig. 2]

In the above test, pH of the leachate from an initial concentration of 8.86 was dropped to 6.7. To identify the solubility of MAP in the leachate affected by pH, 10M NaOH solution was used to raise the pH of the treated leachate from 6.7 to 10.5 and the experimental results are plotted in Fig. 3. When the 10 M NaOH solution was dropped into the treated leachate, pH of the treated leachate was gradually increased, whereas the remaining  $\text{NH}_4^+$ -N concentration was sharply decreased. While pH was increased up to 8.64, the lowest  $\text{NH}_4^+$ -N concentration of 65 mg/l was realised from the remaining  $\text{NH}_4^+$ -N concentration of 210 mg/l (in the case of no pH adjustment). It was thus concluded that the pH range to achieve the minimum MAP solubility in the leachate was around 8.64, say pH=8.5-9.0, which is consistent with the pH range of 8 to 10 found in other studies<sup>8,13</sup> (Schulze-Rettmer, 1991; Zdybieska and Kula, 1991). As shown in Fig. 3, the lowest  $\text{NH}_4^+$ -N concentration began to climb along with the continuous increase of pH almost to 10. It is indicated that beyond the optimum pH of 8.64, the solubility of MAP will increase and the precipitated MAP can be re-dissolved again.

[Fig. 3]

The above experimental results testified the excellent effectiveness of removing  $\text{NH}_4^+$ -N from the leachate by the MAP precipitation. In this precipitation, however, an unwanted by-product, a high amount of salt, was generated in the treated leachate, according to Equation (2). In theory, an amount of 8.375 g of NaCl will be produced when 1 g of  $\text{NH}_4^+$ -N is removed. Such a high concentration of NaCl might affect the treatability of the treated leachate in a following biological treatment process.

*Comparable batch tests with three combinations of chemicals*

To minimise the high amount of salt content in the treated leachate, the other two combinations of chemicals previously mentioned ( $\text{MgO}$  plus  $\text{H}_3\text{PO}_4$  and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  plus  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) were also employed and the precipitation experiments were carried out under similar experimental conditions with the mole ratio of 1:1:1. In these batch tests, the leachate samples with the  $\text{NH}_4^+$ -N concentration of 5,325 mg/l were employed. The experimental conditions and dosage of chemicals used are summarised in Table 3 and 4. The experimental results by comparing  $\text{NH}_4^+$ -N residual concentrations with the additions of different chemicals are shown in Fig. 4. The combination of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  was most efficient for removing  $\text{NH}_4^+$ -N, but generated the highest salt concentration (see conductivity and TDS/FDS in Table 4).

[Table 3]

[Table 4]

[Fig. 4]

The comparison of the conductivity, TDS and FDS in the raw leachate and its treated supernatants by using the three combinations of chemicals are shown in Fig. 5.  $\text{MgO}$  plus 85%  $\text{H}_3\text{PO}_4$  generated the least dissolved salts, while  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  plus  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  generated the least TDS.

The very high salt content generated by using  $MgCl_2 \cdot 6H_2O$  plus  $Na_2HPO_4 \cdot 12H_2O$  may prohibit the activity of bacteria if a conventional biological treatment process is followed. Application of either  $MgO$  plus 85%  $H_3PO_4$  or  $Ca(H_2PO_4)_2 \cdot H_2O$  plus  $MgSO_4 \cdot 7H_2O$  can significantly minimize the salinity of treated leachate. However, some research has been also carried out to enhance the activity of biomass to treat wastewater with high salt intensity (Zhan et al. 1999).

[Fig. 5]

[Fig. 6]

Total and soluble COD concentrations in the raw and the treated leachate were also measured and are shown in Fig. 6. There was no significant reduction in either total or soluble COD in the experiment by using the three combinations of chemicals, which implies that this chemical precipitation technique has a significant selectivity to particularly remove ammonium from leachate, while it is a target of requirement in practice. After chemical precipitation, a biological treatment process can be followed to remove COD as a conventional process. In other words, MAP precipitation may be used as a pre-treatment process to minimise ammonia toxicity before biological treatment.

### **Characteristics of MAP sludge**

By using  $MgCl_2 \cdot 6H_2O$  and  $Na_2HPO_4 \cdot 12H_2O$  with the  $Mg^{2+}:NH_4^+:PO_4^{3-}$  ratio of 1:1:1, the sludge characteristics were studied. To determine the settability of the MAP sludge, a SSV test was

conducted and a SSV curve in the process of sludge settling is illustrated in Fig. 7. It was found that the MAP sludge was settled quite easily. In only 10 minutes, the settled sludge had already reached its maximum compact density. Under this condition, the supernatant was removed and the settled sludge was separated for analyses including CST, SC and DD respectively. The measured results demonstrated CST= 41.4 s, SC= 27%, and DD= 2.05 g/ml or 2050 kg/m<sup>3</sup>. The nature of the MAP sludge indicates that it has a very high sludge density with a fast settling velocity similar to sand or grit and a short CST which allows much easier dewatering than biosludge or flocculent sludge, if dewatering is required. Actually its solids content is much higher than the local standard of SC > 30% required for sludge dumping at a local landfill site. Since this sludge is purely inorganic matter and has very high solids content after sedimentation, it is quite stable and solid enough to be simply dumped at a landfill site without either stabilisation or dewatering treatment. Schulze-Rettmer also reported in 1991 that MAP is a white crystalline powder, not hygroscopic and dries easily in air.

[Fig. 7]

From the above experimental results, the MAP precipitation might be an ideal alternative to traditional technologies for eliminating NH<sub>4</sub><sup>+</sup>-N from leachate. Chemicals consumed in the MAP precipitation process will be the main cost for operation, since its sludge treatment is very simple. From an engineering point of view, some chemical wastes or by-products from chemical industries should be considered as the required chemicals, if possible, so as to lower down the operating costs of MAP precipitation. However, this study was aimed only to evaluate the feasibility of MAP precipitation for ammonium removal from leachate. The results are not

sufficient to estimate the practical costs of both capital and maintenance, until a pilot scale study is carried out later.

## CONCLUSIONS

As a pre-treatment process, the MAP precipitation was technically effective to remove the high  $\text{NH}_4^+$ -N strength of over 5,000 mg/l from the raw leachate collected at the local landfill in Hong Kong. When  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  were employed at the  $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$  mole ratio of 1:1:1, they demonstrated a very satisfactory removal of ammonium; an initial  $\text{NH}_4^+$ -N concentration of 5,618 mg/l contained in the raw leachate was quickly reduced to 112 mg/l within 15 minutes, while the pH producing a minimum MAP solubility was controlled between 8.5 and 9.0. Attention should be given to high salinity formed in the treated leachate during precipitation using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , which may inhibit microbial activity in a following biological treatment process. Other chemical combinations such as  $\text{MgO} + 85\% \text{ H}_3\text{PO}_4$  and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  were conducive to lowering salinity, but they produced lower removal efficiencies of  $\text{NH}_4^+$ -N compared with using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . Moreover,  $\text{MgO} + 85\% \text{ H}_3\text{PO}_4$  generated the least dissolved salts, whereas  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  generated the least TDS. During the MAP precipitation, COD was not significantly reduced. Thus, a biological treatment process may need to be followed to remove COD.

The MAP sludge formed in the precipitation demonstrated an excellent settling feature. Within 10 minutes, the sludge reached its maximum compact density. The settled sludge had the nature of capillary suction time (CST) = 41.4 s, solid content (SC) = 27% and dry density (DD) = 2,050 kg/m<sup>3</sup>, which indicates that the settled MAP sludge can meet the disposal standard at local landfill site without any further treatment.

## **ACKNOWLEDGEMENTS**

The authors wish to thank The Hong Kong Polytechnic University for financial support to this work under the Grant of University Research Committee (PolyU351/607) and under the research project “Area of Excellence – Waste Engineering (336-005)”. Our sincere thanks are also given to the WENT landfill for offering its raw leachate in this study.

## **REFERENCES**

1. Shultz, B. and Kjeldsen, P. Screening of organic matter in leachates from sanitary landfills using gas chromatography combined with mass spectrometry. *Wat. Res.* **20**(8): 965-970 (1986).
2. EPD Environmental Protection Department, Hong Kong Environment, 68-72 (1996).
3. Li, X. Z. and Zhao, Q. L. Inhibition of microbial activity of activated sludge by high strength of ammonia-nitrogen in leachate. Presented in *19th IAWQ Biennial International Conference & Inhibition*, 21-26 June 1998, Vancouver, Canada.

4. Tünay, O., Kabdasli, I. Orhon, D. and Kolçak, S. Ammonia removal by magnesium ammonium phosphate in industrial wastewaters. *Wat. Sci. Technol.* **36**(2-3): 225-228 (1997).
5. Siegrist, H., Gajcy, D., Sulzer, S., Roeleved, P., Oschwald, R., Frischknecht, H., Pfund, D., Mörgeli, B. and Hungerbühler. Nitrogen elimination from digester supernatant with magnesium-ammonium-phosphate precipitation. In: *Chemical Water and Wastewater Treatment II*, Klute R. and Hahn H. H. (Eds.), Spring Verlag, Berlin, 457-465 (1994).
6. Siegrist, H. Nitrogen removal from digester supernatant - comparison of chemical and biological methods. *Wat. Sci. Technol.* **34**(1-2): 399-406 (1996).
7. Zdybiewska, M. W. and Kula, B. Removal of ammonia Nitrogen by the precipitation method, on the example of some selected waste waters. *Wat. Sci. Technol.* **24**(7): 229-234 (1991).
8. Schulze-Rettmer, R. The simultaneous chemical precipitation of ammonium and phosphate in the form of magnesium-ammonium-phosphate. *Wat. Sci. Technol.* **23**: 659-667 (1991).
9. Perry, D. L. and Philips, S. L. *Handbook of Inorganic Compounds*, CRC Press Inc., USA. 235 (1995).
10. Base, J.-H., Kim, S.-K. and Chang, H.-S. Treatment of landfill leachates: ammonia removal via nitrification and denitrification and further COD reduction via Fenton's treatment followed by activated sludge. *Wat. Sci. Technol.* **36**(12): 341-348 (1997).
11. Henry, J. G., Prasad, D. and Young, H. Removal of organics from leachates by anaerobic filter. *Wat. Res.* **21**(11):1395-1399 (1987).
12. APHA *Standard Methods for the Examination of Water and Wastewater*, 16th. ed., American Public Health Association, Washington D. C. (1985).

13. Zdybiewska, M.W and Kula, B. Removal of ammonia nitrogen by the precipitation method on the example of some selected waste waters. *Wat. Sci. Technol.* **24**(7): 229-234 (1991).
14. Zhan X.M., Wang J.L., Wen X.H., and Qian Y. Chock loading caused by high-concentrated salt on activated sludge system, accepted by *Chinese Journal of Environmental Science* (1999).

Table 1. Amount of chemicals added in the 500-ml leachate at various  $Mg^{2+}:NH_4^+:PO_4^{3-}$  mole ratios

$Mg^{2+}:NH_4^+:PO_4^{3-}$	$MgCl_2 \cdot 6H_2O +$ $Na_2HPO_4 \cdot 12H_2O$ (g+g)	$MgO + 85\% H_3PO_4$ (g+g)	$MgSO_4 \cdot 7H_2O +$ $Ca(H_2PO_4)_2 \cdot H_2O$ (g+g)
1:1:0	40.73+0		
1:1:0.5	40.73+35.92		
1:1:0.75	40.73+53.87		
1:1:1	40.73+71.83 (38.61+68.08)*	(7.61+21.94)*	(36.45+18.64)*
1:1:1.1	40.73+79.01		
1:1:1.25	40.73+85.01		
0:1:1	0+71.83		
0.5:1:1	20.37+71.83		
0.75:1:1	30.55+71.83		
1.1:1:1	44.80+71.83		
1.25:1:1	50.91+71.83		

\* Raw leachate has  $NH_4^+-N=5,325$  mg/l (The other leachates have  $NH_4^+-N = 5,618$  mg/l).

Table 2. Characteristics of the raw leachate samples from the WENT landfill

Parameters	Values	Parameters	Values
Physical:		Total PO <sub>4</sub> <sup>3-</sup> -P	16.3
Colour	7,800 (Peaty Brown)	Alkalinity (as CaCO <sub>3</sub> )	13,195
Odour	Slightly ammoniac	Chloride	3,032
pH	8.22	VFA	420
Conductivity	37,000	Potassium	3,920
Turbidity	4,100	Sodium	2,505
Chemical:		Calcium	13.7
Total COD	7,511	Magnesium	93
Soluble COD	6,508	Iron	3.811
BOD <sub>5</sub>	1,436	Manganese	0.182
TSS	784	Nickel	0.365
VSS	654	Copper	0.120
TDS	12,352	Zinc	1.155
FDS	9,420	Chromium	0.553
NH <sub>4</sub> <sup>+</sup> -N	5,000	Cadmium	0.103
		Lead	n.d.(<0.01)

Note: Conductivity in  $\mu\text{mhos/cm}$ ; Colour in Hazen and Turbidity in NTU; all other values except pH in mg/l

Table 3. pH of leachate and the amount of NaOH added with different chemical additions

Precipitant	pH		Volume of 10 M NaOH to adjust pH=9 (ml)
	Raw leachate	Treated leachate	
MgCl <sub>2</sub> ·6H <sub>2</sub> O + Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	8.37	6.88	1.75
MgO + 85% H <sub>3</sub> PO <sub>4</sub>	8.37	5.28	11.3
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O + MgSO <sub>4</sub> ·7H <sub>2</sub> O	8.37	5.13	10.04

Table 4. Experimental results with 3 different combinations of chemicals in MAP precipitation

Chemicals used	NH <sub>4</sub> <sup>+</sup> -N			Conductivity		TDS/FDS		Total/soluble COD	
	Raw	Treated	(mg/l)	Raw	pH=9	(umhos/cm)	Raw	pH=9	(mg/l)
MgCl <sub>2</sub> ·6H <sub>2</sub> O +Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	5,325	530	154	31,000	57,000	14460/ 11,700	54,500/ 49,210	7,113/ 5,522	6,905/ 5,298
MgO +85% H <sub>3</sub> PO <sub>4</sub>	5,325	2,381	1,952	31,000	23,000	14,460/ 11,700	41,120/ 28,540	7,113/ 5,522	5,972/ 4,669
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O +MgSO <sub>4</sub> ·7H <sub>2</sub> O	5,325	2,792	1,398	31,000	27,000	14,460/ 11,700	39,290/ 29,500	7,113/ 5,522	4,772/ 4,246

### **Titles of Figures:**

Fig. 1. Remaining  $\text{NH}_4^+$ -N with the different mole ratios of  $\text{PO}_4^{3-}$

Fig. 2. Remaining  $\text{NH}_4^+$ -N with the different mole ratios of  $\text{Mg}^{2+}$

Fig. 3. Remaining  $\text{NH}_4^+$ -N affected by pH at the  $\text{Mg}^{2+}$ :  $\text{NH}_4^+$ -N:  $\text{PO}_4^{3-}$  mole ratio of 1:1:1

Comb.1:  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ;  
Comb.2:  $\text{MgO} + 85\% \text{ H}_3\text{PO}_4$ ;  
Comb.3:  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Fig. 4. Remaining  $\text{NH}_4^+$ -N in the treated leachate with addition of different chemicals

Comb.1:  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ;  
Comb.2:  $\text{MgO} + 85\% \text{ H}_3\text{PO}_4$ ;  
Comb.3:  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Fig. 5. Conductivity, TDS and FDS in the treated leachate with addition of different chemicals

Comb.1:  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ;  
Comb.2:  $\text{MgO} + 85\% \text{ H}_3\text{PO}_4$ ;  
Comb.3:  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Fig. 6. Total and soluble COD in the treated leachate with addition of different chemicals added.

Fig. 7. SSV curve during MAP sludge settling