

# Novel technique for recovery of sulphur & nitrogen from odorous air at wastewater treatment plant

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## Abstract:

Biofilters used for the conversion of odorous hydrogen sulphide to odourless sulphate in wastewater treatment plants are known to generate large volumes of unusable weakly sulphuric acidic leachate. This paper presents a novel biofilter that produces small-volume and high-concentration sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) as a useful product. The concentrated H<sub>2</sub>SO<sub>4</sub> was produced by washing down the up-flow biofilter with an optimum amount of nutrient solution at pre-determined intervals which created a moisture and pH gradient within the biofilter resulting in an environment at the top favourable for the bacterial conversion of H<sub>2</sub>S, while concentrated sulphuric acid was accumulated at the base. A lab-scale biofilter based on this concept achieved 95 % H<sub>2</sub>S removal efficiency with a maximum H<sub>2</sub>S elimination capacity of 16.3 g/m<sup>3</sup>/h. Only small volumes (1 mL/L reactor/day) of concentrated sulphuric acid (>5.5 M) was produced after 150 days of continuous operation. A pilot-scale trial at a local WWTP not only achieved similar result to that of the lab-scale trial, but the concentrated sulphuric acid also stripped co-contaminant NH<sub>3</sub> from the incoming air resulting in a simultaneous removal of H<sub>2</sub>S and NH<sub>3</sub> with ammonium sulphate as a product in the leachate that can be harvested for further use

**Keywords:** Hydrogen sulphide removal; sulphur and nitrogen recovery; novel biofilter; odour control

## Introduction

Hydrogen sulphide (H<sub>2</sub>S) is considered the most dominant odour from wastewater treatment plants (WWTP). Typical concentrations of H<sub>2</sub>S emanating from WWTPs range from 7 to 590 mg/m<sup>3</sup> that are almost 1000 times the acceptable health limit (Gostelow and Parsons 2000, Chen *et al.* 2006, Lafita *et al.* 2012). There are several existing methods for the removal of odorous compounds from WWTP including incineration, physical adsorbents, chemical scrubbers and biological treatments (Burgess *et al.* 2001, Estrada *et al.* 2011). In recent years, physical and chemical treatments of odours in WWTP have been replaced by biological treatments due to their cost-effectiveness. Among all available biological methods, the biotrickling filters and biofilters are popular systems used for the removal of H<sub>2</sub>S from WWTP.

The main issue associated with biological H<sub>2</sub>S removal is the formation of sulphuric acid by the bacteria leading to an increasingly low pH environment in the biofilter. Not only does low pH decrease the solubility of H<sub>2</sub>S in solution, but the pH can reach a level which is not favourable for the microorganisms. A common strategy to maintain the pH is to trickle water or chemicals such as sodium hydroxide or sodium carbonate down the filter media inside the biofilter. This leads to the formation of leachate containing a low concentration of sulphuric acid, which is considered a waste product that is usually redirected back into the WWTP. The cumulated sulphur within the WWTP ends up in treated wastewater and in biogas when sludge is anaerobically digested.

Although the concentration of H<sub>2</sub>S in polluted air in WWTP is generally low, the volume of the air is high. Depending on the flow rate and concentration of H<sub>2</sub>S being

removed, the amount of sulphur removed from a biofilter could be as high as 17.5 kg of sulphur per day (Rabbani *et al.* 2015). Sulphur is one of the most important raw materials used in industry and sulphur recovery from dilute solutions of sulphuric acid has been considered as a viable source of sulphur (Selim *et al.* 2013). Known industrial processes for the recovery of sulphur from dilute sulphuric acid involve high temperatures and expensive catalysts to produce  $\text{SO}_2$  which is then subsequently converted to concentrated acid (Laursen and Karavanov 2006). Sulphur recovery from the leachate produced in WWTP, which does not involve high amounts of energy or chemicals, would be beneficial to the industry. The sulphur in leachate produced in these processes should be considered a resource rather than a waste product.

Following our successful development of a biochemical ammonia removal process using a reflux biofilter where the amount of water percolating through a biofilter achieving a pH and soluble ion gradient that favour biological ammonia conversion to nitrite at the top of biofilter and spontaneous chemical oxidation of ammonium by nitrite to nitrogen gas (Eckstaedt *et al.* 2016) while producing no leachate, we developed a novel biofilter incorporating a similar strategy to remove  $\text{H}_2\text{S}$  while encouraging the formation of concentrated sulphuric acid as a usable product. This paper aims to describe the overall development of the biofilter system from concept through to lab-scale and subsequent pilot-scale trials at the local WWTP. Extensive detailed information of the biofilter configurations and set up of the lab-scale and pilot-scale trials can be found in Rabbani *et al.* (2016a) and Rabbani *et al.* (2016b) respectively.

### **Principles of the novel biofilter design and operation**

The biofilter system is designed with the aim to produce a minimal amount of leachate (concentrated  $\text{H}_2\text{SO}_4$ ) while maintaining an appropriate moisture content and pH within the biofilter medium suitable within the biofilm for biological removal of  $\text{H}_2\text{S}$ . This is achieved by controlling two operational parameters of the biofilter; (1) optimum amount of water (nutrient solution) delivered into the system and (2) correct interval of the water delivering.

The optimum amount of water is the minimum of water required to add to the biofilter that not only compensates for the volume of water lost due to the difference in relative humidity of the inlet and outlet, but is also sufficient to wash the  $\text{H}_2\text{SO}_4$  (water-soluble  $\text{H}^+$  and  $\text{SO}_4^{2-}$  ions) formed by the biological oxidation of  $\text{H}_2\text{S}$  into the smallest possible volume of leachate leading to a concentrated  $\text{H}_2\text{SO}_4$  solution. This approach is opposite to the prevailing practice of recirculating water over the biofilter and bleeding this off producing leachate that contains dilute sulphuric acid.

The amount and rate of water required to compensate for the volume of water lost in the biofilter can be determined from humidity of the inlet gas flow. Note that humidity of the biofilter outlet gas flow is usually near 100%. When the humidity of a gas entering a system is lower than the humidity of gas coming out, then there will be a net loss of moisture from the system. The actual amount of water lost over time will depend on several factors including the temperature, pressure, flow and humidity of the inlet and outlet gas and the surface area of the liquid in contact with the gas. Estimation of the average water lost can be obtained by simple calculation as shown in Table 1.

**Table 1:** An example of a simple calculation predicting the volume of moisture that can be lost from a biofilter system (*Temperature = 25 °C, Pressure = 1 atm., inlet flow = 1 L/min; Time = 1 hour*)

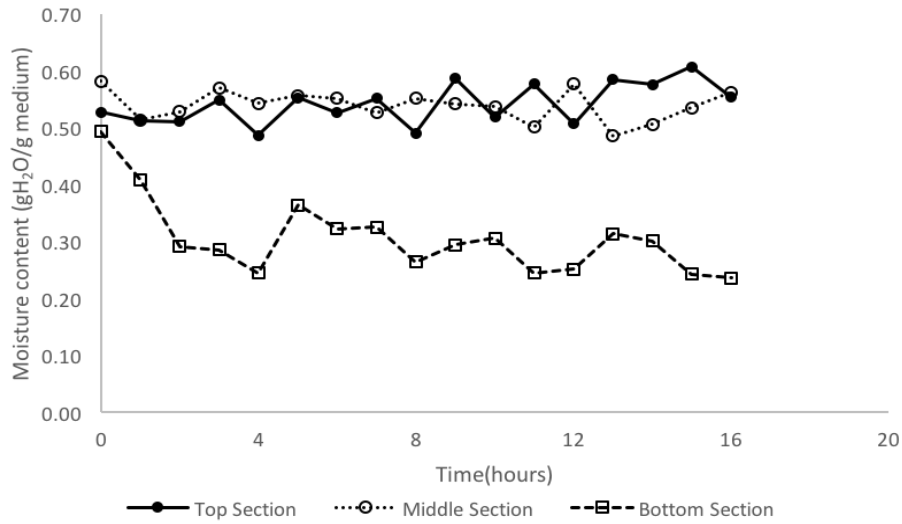
% RH of Outlet			% RH of Inlet			Mass of water lost from system	Rate of volume of water loss from system
%	g/m <sup>3</sup>	mg/min	%	g/m <sup>3</sup>	mg/min	mg/min	mL/h
100	23.02	23.02	40	9.21	9.21	13.81	0.83

To acquire a maximum wash down effect of the water-soluble ions from the filter media with a minimum amount of water, the compensation of the moisture loss in the biofilter is done by intermittently flushing rather than conventional continuous trickling. The minimum volume of water required to flush the water-soluble ions from the filter media at the top to the base of the biofilter varies depending on the type of filter media and biofilter configuration and therefore can only be determined experimentally. Once the minimum amount of water required is obtained, time interval between flush is simply the amount of water required divided by rate of water loss from the system. Flushing the biofilter intermittently creates a moisture and pH gradient within the biofilter resulting in an environment at the top suitable for the bacterial conversion of hydrogen sulphide while sulphuric acid is accumulated at the base.

### Lab-scale biofilter trial

To test the principle of biofilter described above, a lab-scale biofilter using acid resistant PVC piping and polyethylene packing material was set up. The bed volume of the biofilter was 0.926 L and the flow rate was set at 0.9 L/min giving a gas velocity of 23 m/h and an empty bed residence time (EBRT) of 62 s. The details of biofilter configuration and set up can be found in (Rabbani *et al.* 2016a). Based on the dimensions of the biofilter and a preliminary experiment, 3mL of water was the minimum volume of water required to wash down this column and the 3mL of water was determined to be the water lost from the biofilter by evaporation (2.96 mL) during the 4-hour period. As a result, the lab-scale biofilter was operated by flushing 3mL of water (and nutrient) every 4 hours to facilitate the wash down of ions formed in the biofilter.

To examine if this operation would achieve appropriate moisture content in the biofilter, moisture contents of the filter media were monitored for the initial 12-hour period of operation. Results (Figure 1) show that the moisture content of filter media started with all three sections having the similar moisture content (0.5280, 0.5821 and 0.4939 g/g in the top, middle and bottom sections respectively). As dry air entered the column from the bottom, the bottom section started to dry up leading to a decrease in the moisture content in this section. After every 4 hours, when the “top-up” water was added, water trickled down the column and there was an increase in the moisture content of the bottom section. Results show that the bottom section never completely dried out and the top and the middle sections maintained their moisture content during this period providing a steady moisture environment for the biological activity to take place in these sections of the proposed biofilter.



**Figure 1:** Moisture content of filter medium in the 3 sections of the biofilter

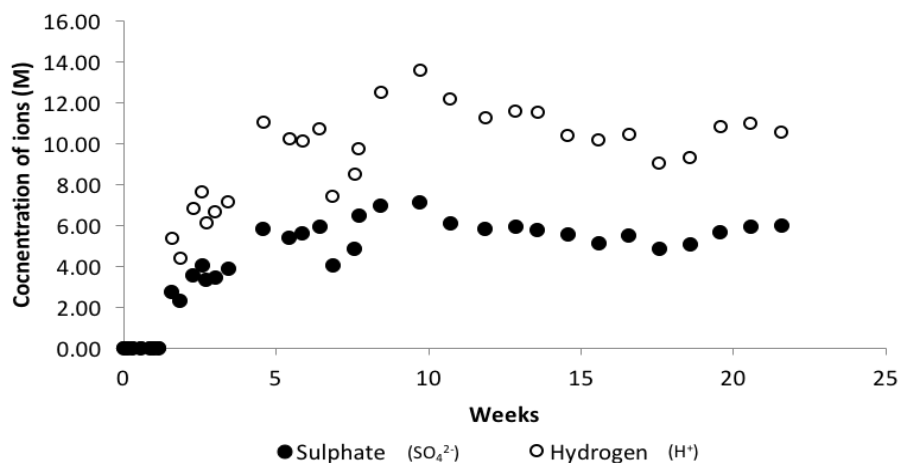
The lab-scale biofilter was operated continuously for 150 days under the parameters presented in Table 2 showing a maximum H<sub>2</sub>S elimination capacity of 16.3 g/m<sup>3</sup>/h and removal efficiency greater than 95 %. The average leachate production was only 1 mL of solution/L reactor/day of H<sub>2</sub>SO<sub>4</sub> with a concentration greater than 5.5 M (Figure 2).

**Table 2** Relevant parameters during the operation of lab-scale biofilter (Rabbani *et al.* 2016a)

	Week 1 – 17	Week 17 – 22
Average H <sub>2</sub> S concentration of inlet air	0.14 g/m <sup>3</sup>	0.28 g/m <sup>3</sup>
Volume of reactor	0.00093 m <sup>3</sup>	0.00093 m <sup>3</sup>
Inlet Flow rate	0.0009 m <sup>3</sup> /min	0.0009 m <sup>3</sup> /min
EBRT	62 s	62 s
Volumetric Load	58 m <sup>3</sup> /m <sup>3</sup> /h <sup>a</sup>	58 m <sup>3</sup> /m <sup>3</sup> /h <sup>a</sup>
Mass loading rate	7.8 g/m <sup>3</sup> /h <sup>b</sup>	16.2 g/m <sup>3</sup> /h <sup>b</sup>
Elimination capacity	7.6 g/m <sup>3</sup> /h	16.3 g/m <sup>3</sup> /h
Removal Efficiency	96%	99%

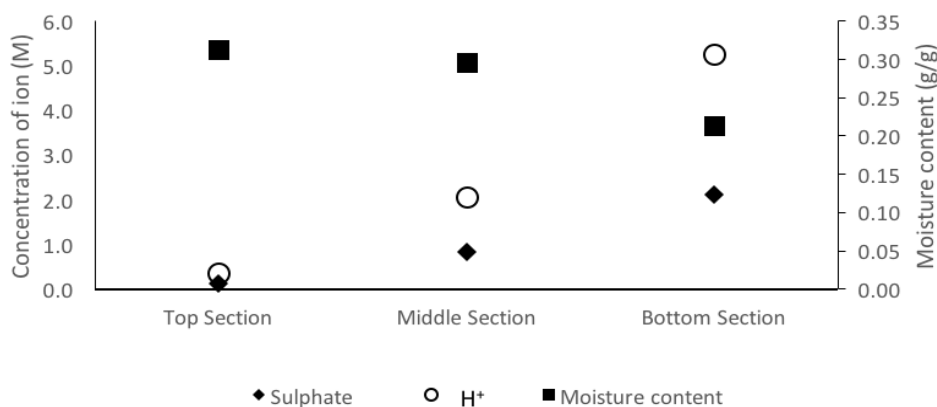
<sup>a</sup> m<sup>3</sup>/m<sup>3</sup>/h refers to m<sup>3</sup> of air flow/m<sup>3</sup> of reactor volume per hour

<sup>b</sup> g/m<sup>3</sup>/h refers to gram of H<sub>2</sub>S/ m<sup>3</sup> of reactor per hour



**Figure 2** Concentration of sulphuric acid in leachate from lab-scale biofilter (Rabbani *et al.* 2016a)

A definite moisture, pH and sulphate gradient was observed (Figure 3). As air with low humidity (44%) entered the biofilter from the bottom, the bottom section was on average drier than the top and middle sections. The top and middle sections of the biofilter had an average sulphate concentration of 0.12 and 0.83 M, respectively, allowing the biological oxidation of H<sub>2</sub>S to continue to take place. The bottom section had an average sulphate concentration greater than 2 M. Detailed evaluation of individual section showed that this section did not remove any H<sub>2</sub>S from the air, all H<sub>2</sub>S removal occurred in the top and middle sections of the biofilter (Rabbani *et al.* 2016a).



**Figure 3** Gradient moisture content and concentration of sulphuric acid over 17 weeks in the different sections of the lab-scale biofilter (Rabbani *et al.* 2016a)

To determine the type of microorganisms in the biofilter, samples of filter media were taken from each section at the end of week 14 for microbial diversity profiling. *Acidithiobacillus* family, which live in low pH environments, were found in all sections of the biofilter, but only the top and middle sections contained organisms identified as being of the *Thiobacillus* family (live in neutral pH environments) (Table 3). As expected, the environment within the biofilter influent the type of microorganism based on the pH and sulphate concentration. While *Thiobacillus* family dominated in the more natural pH of the top section, *Acidithiobacillus* family was the dominant in the low pH of the middle section. Both types of

microorganisms were, however, found to be equally effective in converting H<sub>2</sub>S to H<sub>2</sub>SO<sub>4</sub>.

**Table 3:** Summary of diversity profiling in different sections of the lab-scale biofilter (Rabbani *et al.* 2016a)

	Total sequences	Sequences with <i>Acidithiobacillus</i>	Sequences with <i>Thiobacillus</i>
Top Section	125279	15	186
Middle Section	104996	61	24
Bottom Section	99915	20	0

### Pilot-scale biofilter trial

Following positive results in the lab-scale biofilter trials, a pilot-scale biofilter was set up at a local WWTP (Subiaco WWTP, Western Australia). The WWTP currently uses a series of chemical scrubbers to remove H<sub>2</sub>S and NH<sub>3</sub>. The first scrubber uses 34% sulphuric acid as the scrubbing solution to remove NH<sub>3</sub>, the second scrubber uses 50% sodium hydroxide as the scrubbing solution to remove H<sub>2</sub>S and the third scrubber uses a mixture of 12.5% sodium hypochlorite and 50% sodium hydroxide to remove trace amounts of any other odorous gases before discharging the uncontaminated air into the atmosphere.

The pilot-scale biofilter (details of configuration and operation are available in Rabbani *et al.* (2016b)) was initially set up after the first acid scrubber, where NH<sub>3</sub> in the gas had been removed, to evaluate H<sub>2</sub>S removal and H<sub>2</sub>SO<sub>4</sub> accumulation only (stage 1). The biofilter was operated at this location for 15 weeks at an EBRT of 60 s with an average concentration of H<sub>2</sub>S entering the biofilter at 31.85 ppm (0.04 g/m<sup>3</sup>). After an initial start-up period of only 4 days, the biofilter removed H<sub>2</sub>S from the inlet air at an average removal efficiency of 94.4%. As found in the lab-scale biofilter operation, a clear moisture, pH and sulphate gradient in the biofilter was observed (Table 3) although not as extreme as that of the lab-scale trial. The difference is believed to be the variation in moisture content of air entering the biofilter and temperature fluctuations at the WWTP. The leachate volume produced was still very low. After 15-week operation 163 mL per week of leachate or 1 mL of leachate/L of reactor/day was produced.

Table 3: Gradient of moisture and pH in the pilot-scale biofilter during stage 1 (Rabbani *et al.*, 2016b)

		Top section	Middle section	Bottom Section
Moisture content	g / g*	1.21	1.27	0.99
pH		5.34	4.95	3.67
SO <sub>4</sub> <sup>2-</sup>	mM	1.46	1.79	4.23

\* g/g refers to grams of water per gram of supporting medium

Due to the uniqueness of the biofilter operation described in this study, an extremely high concentration of H<sub>2</sub>SO<sub>4</sub> was accumulated at the base of the biofilter. To determine if this product of biological oxidation of H<sub>2</sub>S, H<sub>2</sub>SO<sub>4</sub> could be used to chemically remove co-contaminant NH<sub>3</sub> from WWTP and possibly replaced the existing acid scrubber, the biofilter was moved and placed prior to the first acid

scrubber. In this stage (stage 2), the biofilter was operated continuously for 7 weeks. The airflow rate at this stage was 50 L/min giving an EBRT of 28 s. The operation and efficiency of the biofilter is summarized in Table 4.

Table 4: Summary of overall results of the novel pilot-scale biofilter operation and efficiency at the local WWTP (modified from Rabbani *et al.*, 2016b)

Average H <sub>2</sub> S concentration of inlet air	31.86 ppm (0.04 g/m <sup>3</sup> )
Average NH <sub>3</sub> concentration of inlet air	1.94 ppm (1.35 mg/m <sup>3</sup> )
Volume of reactor	0.025 m <sup>3</sup>
Inlet Flow rate	0.05 m <sup>3</sup> /min
EBRT	28 s
Mass Loading Rate for H <sub>2</sub> S	5.37 g of S/m <sup>3</sup> /hr.
Mass Loading Rate for NH <sub>3</sub>	0.14 mg of N/m <sup>3</sup> /hr.
Removal Efficiency for H <sub>2</sub> S	91.96 %
Removal Efficiency for NH <sub>3</sub>	100 %

Results of this stage indicated no noticeable change in H<sub>2</sub>S removal efficiency from stage 1. All NH<sub>3</sub> in incoming air was also removed by chemical (H<sub>2</sub>SO<sub>4</sub>) stripping. There was no evidence of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> in the biofilter or leachate confirming that biological oxidation of NH<sub>3</sub> was not occurring (pH too low). Simultaneous biological removal of H<sub>2</sub>S and NH<sub>3</sub> from air by conventional biofiltration have previously shown that it is difficult to maintain the environment favourable to both H<sub>2</sub>S and NH<sub>3</sub> biological oxidation as the oxidation of H<sub>2</sub>S produces an acidic environment in the biofilter which does not promote the growth of ammonia and nitrite oxidising bacteria (Chung *et al.* 2000, Malhautier *et al.* 2003). A combined biological H<sub>2</sub>S oxidation and chemical NH<sub>3</sub> scrubbing described in this study offers a simpler and more effective removal of both H<sub>2</sub>S and NH<sub>3</sub>.

As found in the lab-scale and pilot-scale stage 1 trials, the pH and ions gradient in the biofilter was well maintained throughout the trial period. At the end of the pilot-scale stage 2 trial, the pH and ions in the top section of the biofilter still had an environment favourable for biological oxidation of H<sub>2</sub>S (pH <4.6 and 1.46 mM sulphate) while producing concentrated H<sub>2</sub>SO<sub>4</sub> in the leachate (Table 5). It should be noted that to achieve a simultaneous removal of H<sub>2</sub>S and NH<sub>3</sub> as obtained in this study, the concentration of H<sub>2</sub>S in the contaminated air must be higher than that of NH<sub>3</sub>. Since 2 moles of H<sup>+</sup> can potentially be produced from one mole of H<sub>2</sub>S. The ratio of H<sub>2</sub>S to NH<sub>3</sub> in the contaminated air must be greater than 0.5 to generate sufficient H<sup>+</sup> to remove NH<sub>3</sub> from the air. In this study, the ratio of the amount of H<sub>2</sub>S to NH<sub>3</sub> in the contaminated air from local WWTP was greater than 15, which was more than adequate for the removal of NH<sub>3</sub> in the air.

Table 5: Gradient of moisture, pH and ions at the end of stage 2 (Rabbani *et al.*, 2016b)

		Top section	Middle section	Bottom Section	Leachate
Moisture content	g/g*	1.31	1.18	0.89	-
pH		4.63	3.39	1.51	0.90
SO <sub>4</sub> <sup>2-</sup>	mM	1.46	3.75	10.96	128.39
NH <sub>4</sub> <sup>+</sup>	mM	0.00	0.00	1.2	81.90

\* g/g refers to grams of water per gram of supporting medium

By operating the biofilter as described in this study, concentrated ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) can be obtained as a product. Ammonium sulphate is useful as a fertilizer that provides sulphur and nitrogen to plants as nutrients. At the Subiaco WWTP, the average concentration of NH<sub>3</sub> in the contaminated air with an average flow of 62,500 m<sup>3</sup>/h is 2 ppm. Complete conversion of this ammonia to ammonium sulphate has the potential to produce 17kg of ammonium sulphate per day. Since the solubility of ammonium sulphate in water is 74.4g/100mL, a biofilter system like the one proposed here, which simultaneously removes H<sub>2</sub>S and NH<sub>3</sub> and produces a minimal amount of leachate, can be potentially used to form ammonium sulphate as a solid product. The economic viability of a conversion of the existing chemical scrubber system to a full scale biofilter setup on the principles described in this study can be found in Rabbani *et al.* (2016b).

## Conclusions

It is economically feasible to recover sulphur from H<sub>2</sub>S in contaminated air at WWTP as concentrated H<sub>2</sub>SO<sub>4</sub>. The novel biofilter design and operation proposed in this study was demonstrated in both lab-scale and pilot-scale that by flushing the biofilter with an optimum amount of nutrient solution at a pre-determined interval can create a moisture and pH gradient within the biofilter resulting in an environment at the top suitable for the bacterial conversion of H<sub>2</sub>S while concentrated H<sub>2</sub>SO<sub>4</sub> is accumulated at the base. The cumulated acid at the base of the biofilter can also be used as chemical scrubber for other co-contaminants in the waste air stream. When NH<sub>3</sub> is a co-contaminant, ammonium sulphate is produced and can be harvested as useful product, fertilizer.

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