

Division of
Petroleum

**LEADERS
IN BIOTECHNOLOGY
PRODUCTS**

NT PRODUCT[®]

Odor Control Technology

Controls H₂S – VFAs – Mercaptans

Unique to Atomes



DESCRIPTION

NTP is an environmentally benign, non-toxic and non-biocidal liquid for odor control. Under anaerobic conditions, bacteria metabolize organic carbon compounds to produce malodorous and explosive chemicals. These chemicals, (which include volatile fatty acids (VFA's), hydrogen sulfide (H_2S) and mercaptans) create nuisance odors near the oil drilling.

NTP effectively and economically prevents the production of H_2S and mercaptans, thereby stopping odors from forming thus creating a pleasant living environment. In **petroleum** industry, **NTP** is pumped in water storage tanks in order to oxidize the hydrogen sulphide smell and prevent further generation of H_2S .

NTP is a powdered product that is applied at low concentrations depending upon the initial concentration of hydrogen sulfide gas (H_2S), sulfate and soluble sulfide. This product is generally applied in areas where H_2S are generated such as: water and wastewater treatment plants, pulp and paper mills, petroleum wells, municipality drains and septic systems, grease traps and wherever anaerobic activity is present.

A start-up concentration to prevent the formation of these malodors varies from 1 to 100 ppm.

Unlike other products, NTP:

- Is not a biocide
- Is environmentally-friendly and not toxic
- Prevents the initial formation of these malodors and does not only mask it.
- Oxidize existing H_2S and sulfide.
- Modifies the metabolism of anaerobic bacteria and does not kill these bacteria essential for anaerobic biodegradation, therefore BOD and COD are not affected.
- Prevents the corrosion induced by Sulfate-Reducing Bacteria (SRB).

I- PROTOCOL FOR TESTING

- Take a sample containing SRB bacteria and H₂S odor.
- Measure the amount of soluble sulfate, H₂S gas and soluble sulphide (H₂S gas can be measured by H₂S meter, soluble sulfide and sulfate can be measured by a spectrophotometer using Hach procedures). Please review attached protocols.
- Mix well the sample and split it into containers.
- Close well the containers to promote anaerobic SRB growth.
- In the control container, do not add anything.
- In other containers, add 5 ppm, 25ppm, 50 ppm, 100 ppm, 250 ppm NTP and close very well.
- After 15- 24 hours, measure H₂S gas, soluble sulfide and rotten egg smell. Select the most cost effective concentration that inhibits formation of H₂S and apply it.

NTP works by inhibiting SRB (sulfate reducing Bacteria). These bacteria reduce sulfate SO₄²⁻ to hydrogen sulfide gas (H₂S) and soluble sulfide S₂⁻. To measure the efficiency of NTP product, we have to measure the concentration of soluble sulfide in water and H₂S gas. Usually the presence of NTP in a solution inhibits the formation of H₂S gas and soluble sulfide. Usually in a control sample (ABSENCE OF NTP): The concentration of sulfate decreases due to the activity of Sulfate reducing bacteria, the concentration of H₂S gas increases and the concentration of soluble sulfide increases. In a treated sample with NTP: the concentration of sulfate does not change, there is no formation of H₂S and no formation of soluble sulfide. Also there is the noticeable rotten egg odor reduction in samples treated with NTP.

Soluble sulfides can be measured easily by a Hach or Lamotte method. H₂S gas can be measured by an H₂S meter or a Gastec Unit. Hydrogen sulfide H₂S gas can be measured with the GASTEC by piercing the tape through the hole. [H₂S meter: Type PhD 2 Atmospheric Monitor Model 101 (Biosystems Inc.)].

Soluble sulfide, sulfate and volatile fatty acids were measured with a Hach spectrophotometer DR 2010. To assess sulfide, Sulfide method 813: (Hach; Methylene blue method; 5 to 800 µg/L) adapted from Standard Methods for the Examination of Water and Wastewater was used. Hydrogen sulfide and acid-soluble metal sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue which was measured at 665 nm. A 25 mL of reactors was measured into a sample cell. Deionized water

mL) was measured into a second sample cell (the blank). Sulfide 1 Reagent (1.0 mL) was added to each cell and mixed. Sulfide 2 Reagent (1.0 mL) was added to each cell and mixed. The solution turned blue if sulfide was present. The cells were incubated at room temperature for 5 minutes and sulfide was measured at 665 nm.

To assess VFAs, Method 8196 (Hach; Esterification Method; 27 to 2800 mg/), adapted from The Analyst, 87, 949 (1962) was used. To assess sulfate, Method 8051 (Hach; 2 to 70 mg/L) adapted from Standard Methods for the Examination of Water and Wastewater was used. Procedure is equivalent to USEPA method 375.4 for wastewater.

GC/FID method for determining VFAs concentration

Gas Chromatograph – Hewlett Packard model HP6890. Flame Ionisation Detector (FID). Integration program (HP ChemStations). Column model Supelco 24315, column 15459-01A, type SPB-1000, length 30 m and 0.32 mm internal diameter with a 0.25 μ m thickness film.

GC program: constant flow of 2.5 ml/min of helium. Initial temperature is 120°C constant for 5 minutes, followed by an increase of 15°C/min until 170°C which is kept constant for 5 minutes. The total program consists of 13.33 minutes. Injector temperature: 190°C; detector temperature: 220°C; manual injection: 1 μ L.

Sample preparation: once centrifuged at 13000g for 15 minutes, an amount of 960 μ L of the supernatant was added to 20 μ L solution of 1000 ppm heptanoic acid and 20 μ L solution of hydrochloric acid (37%). This solution was mixed and injected.

OIL DRILLING

I- H₂S scavenger for HCl

NTP in HCl 15% solution

- Use NTP Liquid or NTP powder
- For NTP Powder: make a solution of 50% NTP with water (i.e. Add 100 Kg water to 100 kg NTP powder, to make a NTP aqueous solution).
- Add 1 to 5% NTP aqueous solution in the HCl solution (i.e. HCl 15%) prior to acid job to dissolve the iron sulfide Scale.
- The presence of NTP in HCl solution will oxidize the H₂S gas.
- NTP will not reduce the efficiency of HCl used in dissolving the FeS scale.

II- New Technology for Control of Reservoir Souring by H₂S producing bacteria (SRB)

- Aqueous product added via water injection treats & inhibits reservoir souring, stimulating naturally occurring denitrifying bacteria
- The NRB metabolism oxidizes H₂S in the reservoir to produce harmless hydrogen sulfate, nitrogen and carbon dioxide
- With NTP, NRB grow faster than and dominate SRB (*not kill*)
- Can be significantly more effective at preventing reservoir souring than current chemical methods
- Reducing costs, improving product

III- Application benefits and concern

- Reduces H₂S in reservoir
- Lowers corrosion rate
- Reduces amount of SRB
- Target market is prevention/ remediation of reservoir souring
Not topside biocide replacement - does not prevent biofouling Case by case basis
- Long term solution

Concerns over NRB biofouling downhole

- Must consider downhole injection conditions/ fracturing/ plugging

CASE STUDIES

On-site Experiments

- The study was extended to nine anaerobic facilities (including sites for preliminary experiments) in order to determine the efficiency of the NT product on different samples (open or closed circuits):
- coming from different types of anaerobic wastes (semi-solids, liquids)
- existing under different conditions (climate, additives)
- having different physical-chemical characteristics (organic, inorganic, types of fiber)
- Presenting different odor problems (hydrogen sulfide or volatile fatty acids) with different concentrations of these malodorous compounds in their systems.

A series of experiments were conducted in several plants across Canada and the United States. Since the characteristics of a given wastewater sample change with the age of the sample, on-site experiments were conducted on fresh samples in order to determine the effect of the **NTP** on the removal of volatile fatty acids and hydrogen sulfide.

Many plants (petroleum, pulp and paper, wastewater treatment, compost and water refining) were selected based on the source of odor generation. Several samples with malodorous compounds from primary and secondary wastes, sedimentation basin, cooling tower, equalization basin, primary clarifier, sludge thickener were collected for treatment with **NTP**. Since hydrogen sulfide odor problem is more common than those related to volatile fatty acids, seven plants with hydrogen sulfide odor problems were selected and two plants with volatile fatty acids odors.

Another objective was to determine the reduction of malodors using **NTP** in liquids, semi-solids and pile of solids. Mills with a large volume of wastewater were also selected in order to find out if low concentrations of **NTP** are suitable to remove H₂S. **NTP** was applied to both open and closed pulp and paper mills.

Anaerobic reactor design for treatment of on-site collected samples

The collected samples were placed in polyethylene plastic reactors with a pierced cover. **NTP** was added, mixed and the cover was screwed on each reactor tightly and taped to prevent any exchange of gas from the reactors. Reactors were incubated at a temperature similar to the collection point. Hydrogen sulfide gas in each reactor was measured with the GASTEC by piercing the tape through the hole. Soluble sulfide, sulfate and volatile fatty acids were measured with a Hach spectrophotometer DR 2010.

Methods for on-site Experiments

To assess VFAs, Method 8196 (Hach; Esterification Method; 27 to 2800 mg/l), adapted from The Analyst, 87, 949 (1962) was used. To assess sulfate, Method 8051 (Hach; 2 to 70 mg/L) adapted from Standard Methods for the Examination of Water and Wastewater was used. Procedure is equivalent to USEPA method 375.4 for wastewater. A summary of the methodology and results of the nine experiments are reported in the table below.

Summary of the methodology and results of the nine experiments

Type of mill	Exp. 1 P&P Cartech Canada	Exp. 2 P&P Finch Paper USA	Exp. 3 P&P Domtar Windsor Canada	Exp. 4 P&P Lake Utopia Canada	Exp. 5 P&P Jackson USA	Exp. 6 Waste- water Treatment Canada	Exp. 7 Compost Canada	Exp. 8 Petroleum Oil drilling	Exp. 9 P&P Greenbay USA
Odor	VFA (butyric, Propionic)	H ₂ S	H ₂ S	H ₂ S	H ₂ S	H ₂ S	H ₂ S	H ₂ S	VFA
Collection point	White water loop	Primary & secondary waste	Sedimentation basin & cooling tower	Equalization basin	Primary clarifier & sludge thickener	Retention tank	Composting pile	Oil drilling	Circuit
NT product (mg/L)	100 mg/L	100 mg/L	200 mg/L	25 mg/L	100 mg/L	50 mg/L	200 mg/L	25 mg/L	250 mg/L
Time of experiment	40h	40h	6h15min	8h	48h	96h	48h	24h	3 days
Mill data	-	Presence of sulfate in the system	Presence of sulfate in the system (625 mg/L)	Volume of waste: 5000 cubic meter daily	40 mg/L H ₂ S in the sludge thickener	Flow rate of sludge: 8000 m ³ /d	Semi-solid waste	-	High level of VFAs in mg/L
Volume of samples collected	20 L	100 L in five 20L pails	20 L	20 L	20 L	20 L	20 L	20 L	20 L
Equipments used for measurement	GC	H ₂ S gas detector Spectrophotometer	H ₂ S gas detector Spectrophotometer pH meter	H ₂ S gas detector	H ₂ S gas detector Spectrophotometer	H ₂ S gas detector	H ₂ S gas detector	H ₂ S gas detector	Spectrophotometer
Temperature simulation	Room temp.	30°C	Room temp.	35-39°C	42°C	Room temp.	Room temp.	25°C	Room temp.
Percent % inhibition	Acetic 87% Propionic 84% Butyric 70%	H ₂ S 95.65% S ²⁻ 50%	H ₂ S 54%	H ₂ S 80%	H ₂ S 96% S ²⁻ 76%	H ₂ S 53%	H ₂ S 100%	H ₂ S 85%	VFA 70%

Conclusion of on-site Experiments

NTP was applied on site in different anaerobic processes (Table above). The results of on-site Experiments proved that the **NTP** reduces the formation of VFAs and H₂S in fresh anaerobic samples. Effectiveness of **NTP** product was proved on site in petroleum industry anaerobic processes, pulp and paper.