

**April 20, 2002**

**Laboratory Analysis and Evaluation Report**

**For**

**Apollo Greenzyme<sup>®</sup> in Oilfield Recovery**

**CNPC (China Natural Gas & Petroleum Corporation)**

**Research Institute of China Petroleum Exploration and Development.**

**Beijing, China.**

## Laboratory Studies and Evaluation Report on Apollo Greenzyme®

Water flooding is often applied to unclog and to enhance oil recovery in most oilfields, this practice is especially popular for those oilfields with low permeability.

Traditional methods to unclog most oilfields call for acidifying of the geological formation or by formation-fracturing works. However when dealing with unclogging the geological formation, Apollo Greenzyme® differs entirely from those for applying the acidifying practices.

According to the information supplied from the manufacturer, Apollo Greenzyme® is a protein based, non-living and biological catalyst agent. It has a very high ability to release hydrocarbon compounds (i.e. oil) from the surfaces of any solids.

When Apollo Greenzyme® is pumped into the oil-bearing formation, it can set free those oily crystals and agglomerates building-up near the bore head of an oil well, it can also release those aged wax and asphaltene from the sandy solid surfaces.

In so doing, Greenzyme® can change the wettability of the sandy formation from an oil-wetted basis to a water-wetted basis. Such a change can reduce the oil flow resistance within the porous geological formation, it can also help the formation to accept an increase capacity for water-flooding, all these can result in solving the clogging problems for water-flooded wells, as well as in increasing oil production for oil-produced wells.

From our studies of Greenzyme® through contact angle changes and evaluation, through oil-releasing capability tests and through core sample unclogging experiments, we can assess the effect of Apollo Greenzyme® on oil well applications. Our experimental methods and their results are as follow:

## Experimental methods

### 1) Contact angle tests:

Raw materials: Quartz plate (i.e. SiO<sub>2</sub>).

Crude oil from Gudong, Shengli Oilfield, China, i.e. about API 18.

N-pentane (i.e. C<sub>5</sub>H<sub>12</sub>), and chromic acid washing fluid.

Instrument: CS-2 contact angle instrument.

#### Procedures:

- a) Cleaning quartz plate: Chromic acid wash and rinse thoroughly with distilled water, followed by oven-baked dry. Take the dried quartz plate, release one single drop of water on its surface, observe to see if the water drop spread out evenly onto the surface, if not, repeat this washing cycle again until success.
- b) In a closed container, immerse the cleaned quartz plate into 20 ml of crude oil for 3 days aging-process; at the beginning of this aging procedure, for every 12 hours, add 10 ml of n-pentane to the container, for a total of 60 ml n-pentane in 3 days.
- c) After the aging period, take out the quartz plate and rinse the plate with n-pentane, then baked dry the quartz plate at 80-95 degree C oven until completely dried, then place the plate inside a desiccator for later use.
- d) Release one drop of water, or one drop of various % concentration of Greenzyme™ on the surface of the quartz plate, use CS-2 contact angle instrument to detect changes of contact angles on the surface.

2) **Oil-releasing capability tests:**

Raw materials: Quartz sand (60-120 mesh), crude oil.

Instrument: WAOR Instrument, i.e. water absorbing, oil rejecting instrument.

Procedures:

- a) Place 1.5 Kg of quartz sand inside an oven, set temperature at 120 degree C and bake for 2 hours, then let it cool back to room temperature, put the sand sample inside a desiccator for later use.
- b) Take 1 Kg of the quartz sand and well stir mix it with 125 g of crude oil, place the mixture inside an oven at 85 degree C, and bake them for 24 hours. Then cool the mixture to room temperature, the place them inside a desiccator for later use.
- c) Oil-releasing capability tests:

Take 5 grains of the quartz sands (i.e. the one after oven baked from the previous steps) and place them inside the WAOR instrument, then add the candidate testing fluids, place them inside a constant room temperature box for observation, take time measured readings for oil releasing quantities.

### 3) **Core sample unclogging experiments:**

Raw materials: NS, natural sand, i.e. natural core sample with low permeability sands.

QS, quartz sand, i.e. filler material using quartz sands.

OCW, oil-contaminated water, i.e. man-made oil contaminated water, or water with 10% crude oil.

#### Procedures:

a) Core sample go through complete vacuum suction, then let saturated with water soak; measure water penetration rate and the pumping pressure required to pump through the core sample.

b) Force pumping OCW the core samples as below:

NS core sample: 0.3 ml / min pumping rate, let the crude oil adhere onto the surfaces of the sample to create a uniform cross-sectional clogging.

QS core sample: 1.0 ml / min pumping rate, not only let the crude oil adhere onto the surfaces of the sample to create the initial clogging, but also let the free migration of the solid particles inside the core to create the secondary clogging as well.

c) Pump one unit (i.e. one equal volume size as the core sample) of 10% **Greenzyme®** into core sample for all tests.

d) Place all tested materials at a constant room temperature for 48 hours, then start pumping salt water at 0.3 ml / min rate to test various pressure changes required for pumping.

**Note: all of the above experimental tests were done using Gudong crude oil from Shengli Oilfield of China.**

## Experimental results:

### 1) Contact angle tests and results:

**Table 1.** Effect of contact angle changes versus time using 10% Greenzyme®.  
(All contact angle values recorded in degrees.)

<b>Time (minutes)</b>	<b>0</b>	<b>3</b>	<b>5</b>	<b>7</b>	<b>10</b>
<b>Salt Water (degree)</b>	<b>125<sup>0</sup></b>	<b>123<sup>0</sup></b>	<b>123<sup>0</sup></b>	<b>120<sup>0</sup></b>	<b>115<sup>0</sup></b>
<b>10% Apollo Greenzyme™ (degree)</b>	<b>96<sup>0</sup></b>	<b>72<sup>0</sup></b>	<b>62<sup>0</sup></b>	<b>50<sup>0</sup></b>	<b>42<sup>0</sup></b>

**Table 2.** Effect of various % Greenzyme® concentrations versus  
changes in contact angle variations  
(all values recorded on 10 minutes time delay measurement.)

<b>Greenzyme® Strength ( % )</b>	<b>0%</b>	<b>5%</b>	<b>10%</b>	<b>20%</b>	<b>30%</b>
<b>Contact Angle (degree)</b>	<b>125<sup>0</sup></b>	<b>56<sup>0</sup></b>	<b>42<sup>0</sup></b>	<b>35<sup>0</sup></b>	<b>32<sup>0</sup></b>

*Table 1 & 2 cont.*

- Apollo Greenzyme® possesses a profound capability to change the contact angle on solid-liquid wettability. Even on a very short period of time (i.e. less than 5 minutes), Greenzyme® can thoroughly change the solid quartz from an oil-wetted surface to a water-wetted surface, with the longer the time, the contact angle proceeds further towards water wettability changes.
- Greenzyme® strength between 10% and 30% shows remarkable efficiency in this aspect.

2) **Oil-releasing capability tests and results:**

**Table 3.** Relationship of oil-releasing capability versus time using 10% **Greenzyme®**.

<b>Time ( Hour )</b>	<b>0.3</b>	<b>0.5</b>	<b>1.0</b>	<b>3</b>	<b>5</b>	<b>10</b>	<b>24</b>	<b>48</b>	<b>72</b>
<b>Salt Water ( % Oil Recovered )</b>	<b>0.3%</b>	<b>0.7%</b>	<b>0.9%</b>	<b>1.5%</b>	<b>1.8%</b>	<b>2.3%</b>	<b>2.8%</b>	<b>3.0%</b>	<b>5.1%</b>
<b>10% Greenzyme® ( % Oil Recovered )</b>	<b>8.5%</b>	<b>12.4%</b>	<b>16.6%</b>	<b>23.5%</b>	<b>28.6%</b>	<b>33.5%</b>	<b>46.8%</b>	<b>48.6%</b>	<b>49.1%</b>

- Before addition of 10% Apollo **Greenzyme®**, salt water alone shows a very low effect to release oil from the test samples, even after 24 hours of time; salt water alone can only recover 2.8% of crude oil.
- After addition of 10% **Greenzyme®** to the same tests, the oil-releasing capability greatly improves; over 40% of crude oil is recovered after 24 hours of time. This fact indicates Apollo **Greenzyme®** has a much higher capability to release crude oil from any surfaces of oil-bearing sands.

3) **Core sample unclogging experiments and results:**

**Table 4.** Low permeability core sample unclogging experiments using NS (i.e. natural sand.)

Core diameter ( cm )	Initial H <sub>2</sub> O penetration rate	Initial H <sub>2</sub> O pumping pressure ( MPa )	Initial oil penetration rate	After 10% Greenzyme® addition, pumping pressure ( MPa )	After 10% Greenzyme® addition, oil penetration rate
7.85	8.6	2.86	2.1	1.12	6052

**Table 5.** Experimental results using QS (i.e. quartz sand) filler materials as core samples.

Core diameter ( cm )	Initial H <sub>2</sub> O penetration rate	Initial H <sub>2</sub> O pumping pressure ( MPa )	Initial oil penetration rate	After 10% Greenzyme® addition, pumping pressure ( MPa )	After 10% Greenzyme® addition, oil penetration rate
13.55	8504	2.35	18	1.45	55.6

*Table 4 & 5 cont.*

- For natural core sample using NS i.e. natural sand, oil-bearing water is pumped at a slower rate, migration of solid particles inside the core is small, this is mainly because the crude oil in the feeding water adhered to particle's surfaces to create a drop in fluid penetration rate, the pumping pressure requirement continued to rise rapidly.
- For core sample using the loosely filled quartz sands, because the fluid pumping rate is faster, both the adhesion of crude oil onto the surfaces of the particles and the migration of individual grains create a high pressure drop for the feed pump. From these experiments above, they all clearly indicate Apollo Greenzyme® has excellent unclogging properties for both of these two cases.

**Applying a 10% Apollo Greenzyme® to the tested sample and wait for 48 hours, the required pumping pressure to continue water-flooding the core sample will required a much lower pumping pressure.**

## Conclusions

- 1) From contact angle tests, oil-releasing capability tests and core sample unclogging experiments, they all clearly indicate Apollo Greenzyme® can easily release crude oil from the surfaces of oil-bearing sands, changing these sands from oil-wetted surfaces to water-wetted surfaces. This change will succeed to unclog those oil wells with difficulties in water flooding drive.
- 2) For those wells with low water permeability rate, which require higher water-flood pumping pressure, this is mainly due to crude oil component breaking-down and building-up barriers inside the geological formation, using Apollo Greenzyme® can produce a very good result.
- 3) Apollo Greenzyme® can be used extensively in oilfields for:

**Water-flooding wells:** for reducing pressure drop and for increasing water-pumping capacity.

**Oil producing wells:** for formation unclogging and for increasing oil production.

**Greenzyme® is a registered trademark for  
Apollo Separation Technologies Inc. of Houston, Texas USA.**