Stability of Super Absorbent Polymers in Sodium Nitrate - 16222

Martin Matushek
M² Polymer Technologies, Inc.
martin@m2polymer.com

ABSTRACT:
The stability of two different chemical types of cross-linked super absorbent polymers has been explored using a surrogate waste of 3M Sodium Nitrate ($NaNO_3$) that had pH adjusted using concentrated Nitric Acid (HNO_3) to pH of 1, 2, 4 and 6. Tests showed both types of polymer gelled the surrogate waste liquids. On-going stability tests revealed that there was no breakdown of the waste form after 11 months and no release of free liquids.

INTRODUCTION:

M² Polymer Technologies has been in existence since January 2000 and markets a variety of super absorbent products under the "Waste Lock®" brand. In October of 2014, we were contacted by personnel of the Los Alamos National Laboratory (LANL) to see if there was any data that showed the stability of these sorts of super absorbent polymers to strong oxidizing agents. The question arose after waste drums from LANL exploded underground at WIPP. LANL explained that it appeared that waste with high levels of nitrates was solidified first using conventional cat litter (i.e. Sodium Bentonite clay) but that at some point, a switch was made to a "natural" cat litter made from some sort of plant fibers. It appears that this waste reacted with the nitrates and/or underwent radiolysis to form gases that caused the drums to explode.

We explained to the LANL people that, while we had extensive experience with many types of LLRW and other chemical contaminants, we had never specifically tested the polymers with strong oxidizing agents. We thought that this work may yield some interesting data and so we undertook this project out of intellectual curiosity.

After some discussion with LANL people who said that there was quite a range of waste forms in the damaged drums, they agreed that a good surrogate waste base would be to use a 3M Sodium Nitrate solution and then adjust pH to the range of 6 down to pH of 1.

DESCRIPTION:

This simple and straight-forward study used the following materials & supplies:

- Sodium Nitrate ($NaNO_3$) – ACS Grade from Alfa Aesar
- Nitric Acid (HNO_3) – ACS Grade from Amresco
- Distilled water
- pH Meter (Jenco pH 630 VisionPlus)
- pH calibration Buffer Solution (Fisher Chemicals)
- Stirring plate with magnetic bar
- Analytical scale (AccuLab/Satorius Group)

Absorbency Cuvettes (1" X 1" diameter w/ 100 mesh stainless bottom)
Petri Dishes
Glass beakers
Glass jars 6 oz (180 cc) with plastic lids
Eyedropper
Waste Lock® 770 superabsorbent polymer
Waste Lock® PAM/Type S (200-800 µm)

The two Waste Lock® polymers were tested as they are very distinct chemically and in terms of performance. Both products have a particle size distribution of 200 to 800 microns. The products also use different cross-linking agents.

Waste Lock® 770 is a sodium polyacrylate homo-polymer made via gel polymerization.

Waste Lock® PAM is a potassium co-polymer of acrylic acrylamide made via solution polymerization. This polymer generally yields higher absorbency results in more aggressive liquids (i.e. high or low pH, high conductivity).

One liter batches of a 3M Sodium Nitrate solution were made by adding 254.97 grams (3 X MW of 84.99 g/mole) to 1000 grams of distilled water. The solution was stirred with a magnetic bar.

Superabsorbent polymers absorb by means of a diffusion gradient. This means that the higher the cationic concentration (i.e. conductivity), the lower the absorbent performance. In Deionized water, one gram of either Waste Lock® polymer will absorb about 500 grams of water. Jump to 1% NaCl and one grams absorbs about 55 grams of this saline solution.

Our first step was to determine Free Swell (EPA 9095 Paint Filter Test) Absorbency Ratios for both polymers under a range of pH conditions. We added small (0.15-0.20 gram) samples of a polymer to each cuvette. Then 100 ml aliquots of the 3M $NaNO_3$ solutions were taken and pH was adjusted accordingly. Two cuvettes were then placed in a petri dish and 50 mls of the pH-adjusted test liquid were added. Samples sat and soaked for 60 minutes. Thereafter, they were weighed and the liquid absorbency was calculated and averaged between the duplicate samples.

Results are as follows:

TABLE I. Free Swell Absorbency Test Results

Free Swell Absorbency in 3M $NaNO_3$ Solution	Waste Lock® PAM/Type S	Waste Lock® 770
At pH = 6	25.7 g/g	22.9 g/g
At pH = 4	24.5 g/g	20.4 g/g
At pH = 1	22.8 g/g	18.6 g/g

Since this surrogate waste is an aggressive liquid, for the stability study, we elected to apply DOE "safety margin dosing" and to employ a conservative absorbency ratio of 10 g/g (10 grams of polymer sorbent in 100 grams of surrogate waste).

Aliquots of 200 grams of 3M $NaNO_3$ solution were taken and pH was adjusted downward with drops of concentrated HNO_3. Each 200 gram aliquot was split between two jars with 100 grams apiece. Then 10 grams of each of the two polymers were added to a given jar. At the conclusion, there were eight jars as follows:

Waste Lock® 770 (10 grams/100 grams surrogate) at pH = 1, 2, 4 and 6.
Waste Lock® PAM (10 grams/100 grams surrogate) at pH = 1, 2, 4 and 6.

All jars were solidified within five minutes of sorbent addition. We then monitored and observed the jars for any signs of gel breakdown, gas formation or free liquids.

DISCUSSION:
Results in the early days of this stability test showed no degradation of the polymer gels in any of the jars and no visible gas formation and no free liquids.

As of this writing in November of 2015 after 10 months, all eight jars contain dry, stabile gels with no free liquids. Recent photos are attached:

Figure 1: Photo of Waste Lock® 770 Jars After 11 months

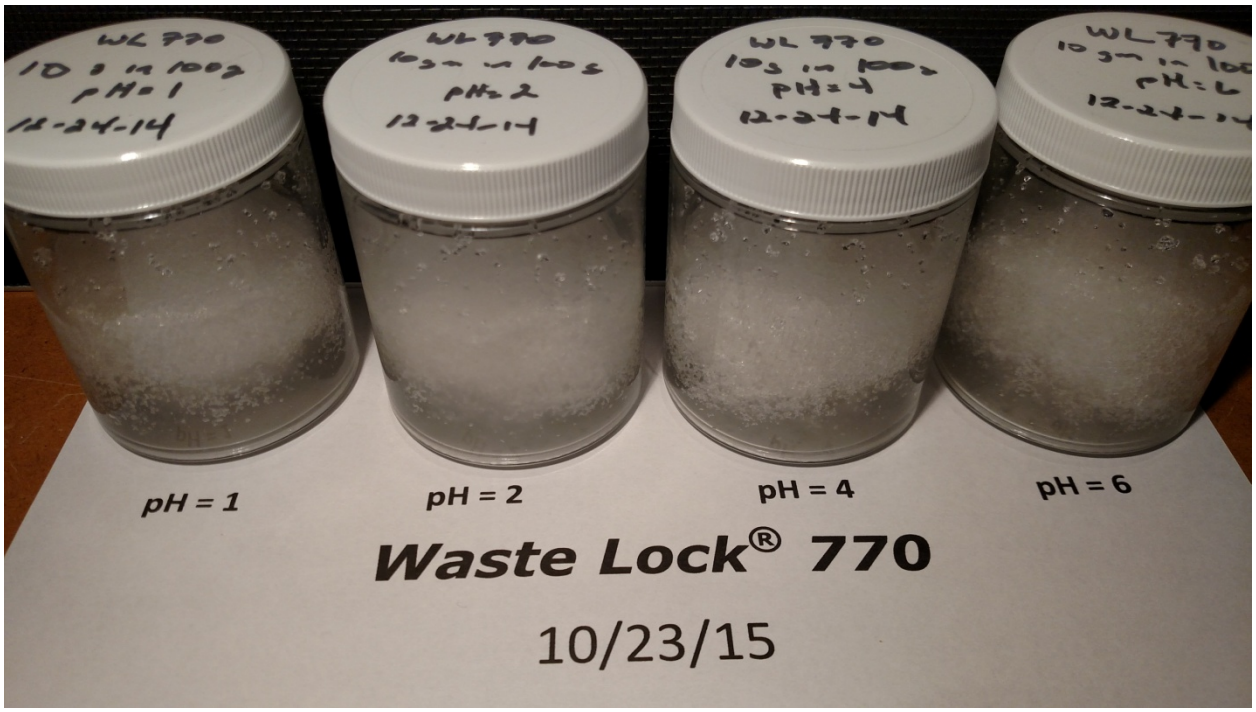

Figure 2: Photo of Waste Lock® PAM/Type S Jars After 11 months

CONCLUSIONS:

Tests show that both polymers – Waste Lock® 770 (Sodium polyacrylate) and Waste Lock® PAM (Acrylic-acrylamide co-polymer) offer solidified, stabile gels with a strong oxidizing waste (3M Sodium Nitrate ($NaNO_3$)) through a range of acidic pH. Tests showed both types of polymer gelled the surrogate waste liquids – although the PAM version offered 10-20% higher absorbency performance in this aggressive waste. On-going stability tests revealed that there was no breakdown of the waste form after 11 months and no release of free liquids.