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3M™ Neutron Quench*: Compounds with Substantial Water Solubility and Boron Content

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Abstract

Of the two naturally occurring isotopes of boron (^{11}B 80%, ^{10}B 20%), ^{10}B is a good neutron absorber with a thermal neutron absorption cross section of ~3800 barns. The ability to absorb thermal neutrons while producing benign reaction products makes boron an ideal atom to aid in the control and arrest of the fission reaction in nuclear power reactors. In current practice, boric acid and sodium pentaborate are commonly used as neutron absorbers in the water regime of active and passive safety systems.

3M™ Neutron Quench compounds have been developed to be applied in situations where criticality control needs exceed normal control methods. In this type of situation these compounds have several advantages over commonly used neutron absorbers like boric acid:

- **Boron Content:** Compounds contain up to 80 wt% boron compared to 16 wt% for boric acid and sodium pentaborate
- **Solubility:** >16 g B/100 g solution compared to 0.6 g B/100 g solution for boric acid at 25°C
- **pH neutrality:** Compounds demonstrate pH neutrality even in concentrated solutions
- **Stability:** Compounds are stable as solids at temperatures greater than 500°C
- **Corrosiveness:** Electrochemical corrosion rate studies have indicated that these compounds are significantly less corrosive than boric acid

Use of 3M™ Neutron Quench can lead to reduction in emergency shutdown pool size, reduce or remove the necessity for pool heating and heat tracing of lines, allow for more rapid introduction of the absorber in emergency situations or be used in other applications where significant neutron control is necessary.

Keywords: shutdown, boron, water chemistry, enriched boron

1 Introduction

Of the two naturally occurring isotopes of boron (^{11}B 80%, ^{10}B 20%), ^{10}B is a good neutron absorber with a thermal neutron absorption cross section of ~3800 barns. The ability to absorb thermal neutrons while producing benign reaction products makes boron an ideal atom to aid in the control and arrest of the fission reaction in nuclear power reactors. Boric acid, both natural and isotopically enriched, is recommended by the International Atomic Energy Association (IAEA) to be part of the water chemistry regime in active and passive safety systems.[1] The use of boric acid in this type of application has known detriments that must be strategically mitigated. An example of the problems that can come from boric acid use was found in early March 2002 at the Davis-Besse nuclear power station in Oak Harbor Ohio.[2] At this plant it was discovered during an inspection that between 650 and 980 cc of metal had corroded and been flushed away from the reactor pressure vessel head, leaving only a thin layer of steel cladding about 7.6 mm (0.3 in.) thick. This incident shows that boric acid, while a weak acid (pH of 3-4 for concentrated solutions), can cause significant damage to power plant construction materials under elevated pressure and temperatures.

Boric acid is also commonly used in emergency situations. In November of 2011 the Tokyo Electric Power Company (TEPCO) detected the possible presence of radioactive gases from inside the primary containment vessel (PCV) of unit 2 from the tsunami damaged Fukushima Daiichi Nuclear power station in Japan.[3] In response to this detection 10 tons of boric acid solution (water containing 480 kg of boric acid) was injected into the PCV. In this and other emergency situations, using 3M™ Neutron Quench compounds could significantly decrease the amount of material needed due to their high boron content, decrease the overall volume needed due to their high solubility, and be far less damaging to commonly used containment materials.

2 Experimental

2.1 Boron Content

With a chemical formula of $B(OH)_3$, boric acid has one boron per mole of boric acid and is 17.48 % by weight when natural abundance isotopic distribution is assumed. To determine the boron in these compounds the level of hydration was measured by thermogravimetric analysis. Tests were performed on a TA instrument TGA Q500, using 8 to 10 milligrams of compound. Samples were heated under nitrogen using a heating ramp of 10°C/min from room temperature to over 600°C. Mass loss occurring around 100°C was assumed to be due to water loss and the boron content of the "as isolated" material was readily calculated. This calculated level of hydration was used to determine the amount of boron present. With the known boron content solubility, pH and corrosion tests could be performed on a boron content basis. The TGA data is provided in Table 1.

Compound	Weight % Loss in Temperature Ranges				
	30-100°C (%)	100-200°C (%)	200-300°C (%)	300-400°C (%)	400-500°C (%)
1	3.02	23.13	35.21	35.64	36.03
2	1.62	7.66	8.17	8.00	8.21
3	4.86	5.50	5.58	4.53	3.34
4	7.15	21.45	42.59	42.61	42.88
5	0.38	19.76	24.00	24.11	25.55
6	3.82	5.18	5.63	5.53	4.37

Table 1: TGA data of 3M™ Neutron Quench Compounds 1-6

2.2 Solubility

The solubilities of 3M™ Neutron Quench compounds were measured using the procedure outlined by the Organisation for Economic Co-operation and Development (OECD).[4] The compound (3.0 g) being tested was placed in an appropriately sized graduated cylinder and water was added in small aliquots (1 to 2 mL) from a calibrated pipette. The solution was then stirred for ten minutes. If there was undissolved material present more water was added until all the material was in solution. This test was performed multiple times for each compound at four different temperatures (0°C, 22°C, 40°C and 60°C). The same test was also performed on boric acid as a test control. The solubility data is shown in Table 2.

Temperature (°C)	Compound Solubility (g Boron/100 g water)							
	1	2	3	4	5	6	Boric Acid	Boric Acid Literature
4	16.5	13.5	6.2	16.7	13.7	6.8	0.5	0.5
22	27.9	20.5	8.1	27.9	22.2	9.4	0.8	0.8
40	46.3	35.6	15.8	41.3	32.9	20.4	1.3	1.4
60	75.6	55.2	25.0	64.9	48.2	33.0	2.1	2.3

Table 2: 3M™ Neutron Quench Solubility in Water

2.3 pH Testing

The pH of each compound was measured using a Fisher pH/Ion 510 pH meter calibrated in accordance with the Fisher Science Education pH/Ion 510 manual. The calibration curve consisted of three standards with pHs of 4.01, 7.00, and 10.01. The standards were Orion Application Solutions purchased from Thermo Scientific and certified traceable to NIST standard reference material. The amount of each compound used was boron weight equivalent to a concentrated boric acid solution at room temperature. All materials were dissolved in degassed deionized water. The pH of each solution was measured before the compound was added, upon compound addition, after stirring for 5 minutes, 10 minutes, and 15 minutes. Results of pH testing are shown in Table 3.

Time	Compound pH						
	1	2	3	4	5	6	Boric Acid
Before addition	6.47	6.48	6.44	6.55	6.48	6.50	6.5
5 Minutes	6.77	6.70	6.92	6.68	6.83	6.86	4.2
10 Minutes	6.80	6.81	6.98	6.73	6.91	7.03	3.9
15 Minutes	6.79	6.81	6.98	6.72	6.90	7.03	3.8

Table 3: 3M™ Neutron Quench pH Testing

2.4 Electrochemical Corrosion Testing

The electrochemical corrosivity of the compounds was measured using a Princeton Applied Research VersaSTAT 4 potentiostat/galvanostat equipped with a 15 cm long platinum counter electrode and a silver chloride single junction 14/20 adapter reference electrode, both from Pine Research Instrumentation. Type 304 stainless steel coupons purchased from Rohrback Cosasco Systems were used as the working electrodes. The amount of each compound used was boron weight equivalent to a concentrated boric acid solution at 22°C. An area of 2.55 cm × 1.25 cm × 0.15 cm of the steel coupon was submerged in 150 ml of each compound's solution. The galvanic corrosion rate (I_{corr}) was evaluated using a Tafel plot which plotted the Current (A) versus Potential (V).[5] The Tafel plot was carried out by using an initial potential of -0.25V and final potential of 0.25V. The scan properties were a step height of 5 mV, a step time of 1 second and 101 total points collected. This test was performed at both 22°C and 80°C. A summary of results is shown in Table 4.

Compound	I_{corr} at 22°C (µA)	I_{corr} at 80°C (µA)
1	8.887	20.678
2	4.707	23.613
3	7.005	21.047
4	3.528	22.384
5	5.787	23.590
6	3.209	20.418
Boric Acid	20.387	39.988

Table 4: Electrochemical Corrosion of 3M™ Neutron Quench

3 Results and Discussion

3.1 Boron Content

Preliminary TGA data shows that the 3M™ Neutron Quench compounds maintain some level of hydration as a result of the synthesis. All compounds experience some mass loss around 100°C as expected for a weak hydrate (Figure 1). However, the compounds remain at least 50% boron by weight as the isolated powders. Efforts are being made to develop synthetic methods that result in anhydrous material. However, hydration is not an issue given the expected use of the compounds will be as part of an aqueous system.

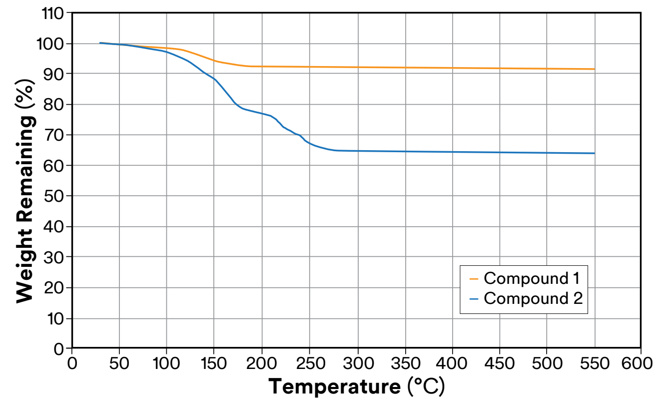

Figure 1: Example TGA Charts for Compounds 1 and 2.

The TGA analyses show that these compounds are stable as solids beyond 500°C. While this does not demonstrate stability under emergency reactor conditions, it is an important first step in the assessment of these compounds. Evaluation of these compounds under conditions representative of an emergency shutdown situation is ongoing.

3.2 Solubility

Results of solubility testing are shown in Figure 2, which demonstrates that all 3M™ Neutron Quench compounds possess significantly higher solubility in water at every temperature investigated.

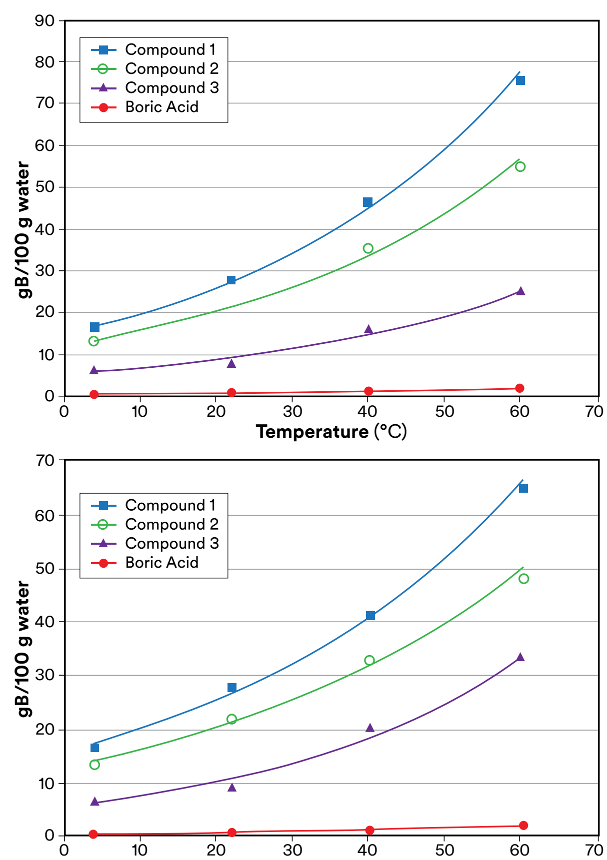

Figure 2: 3M™ Neutron Quench Solubility Compared to Boric Acid. Compounds 1-3 (top) and Compounds 4-6 (bottom).

At 4°C boric acid has a boron solubility of about 0.6 g B/100 g water compared to a range of 6 g B/100 g water to 16 g B/100g water for these novel compounds. This is a potential 30 fold increase in boron content for solutions containing the same amount of water compared to boric acid. This solubility ratio holds as the temperature is increased. At 60°C compounds 1-6 range from 25 g B/100 g water to over 75 g B/100 g water. In terms of solution boron content this is 10 to 32 times the boron content of a saturated boric acid solution at the same temperature (2.3 g B/100 g water).

This data clearly demonstrates the exceptional water solubility of these compounds and resulting boron content. This is a fundamental consideration in emergency shutdown situations. With these levels of boron solubility the volume of solution needed to reduce the neutron flux to safe levels is drastically reduced when compared to boric acid or sodium pentaborate systems. This increased solubility and boron content could allow for a significantly smaller emergency pool footprint. Furthermore, the need for heated pools and heat traced lines in emergency safety systems that are necessary to prevent boric acid crystallization may be eliminated or significantly reduced.

3.3 pH Neutrality

The pH of 3M™ Neutron Quench solutions is compared to boric acid in Figure 3. The concentration of compounds 1-6 was tailored to provide the same concentration of boron compared to a saturated boric acid solution. The data shows that upon addition of any of the Neutron Quench compounds there is a slight pH increase compared to the deionized water used in the testing but remains neutral. This contrasts sharply to the significant drop in pH to 3.8 for a saturated boric acid solution.

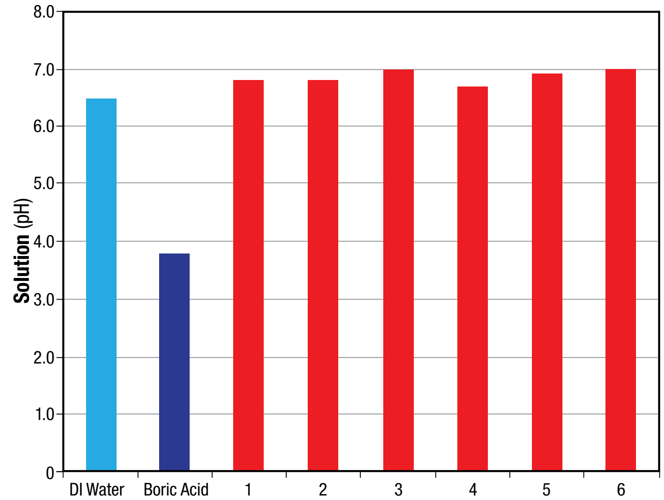

Figure 3: pH of 3M™ Neutron Quench

The synthesis of these compounds involves strongly basic chemicals. The general increase in pH that is shown in Figure 3 for these compounds is evidence of the need to further reduce residual base levels from the synthesis procedure rather than a reflection of the seemingly basic nature of these compounds. Indeed, it is expected, and the data supports that these compounds are neutral in their isolated state.

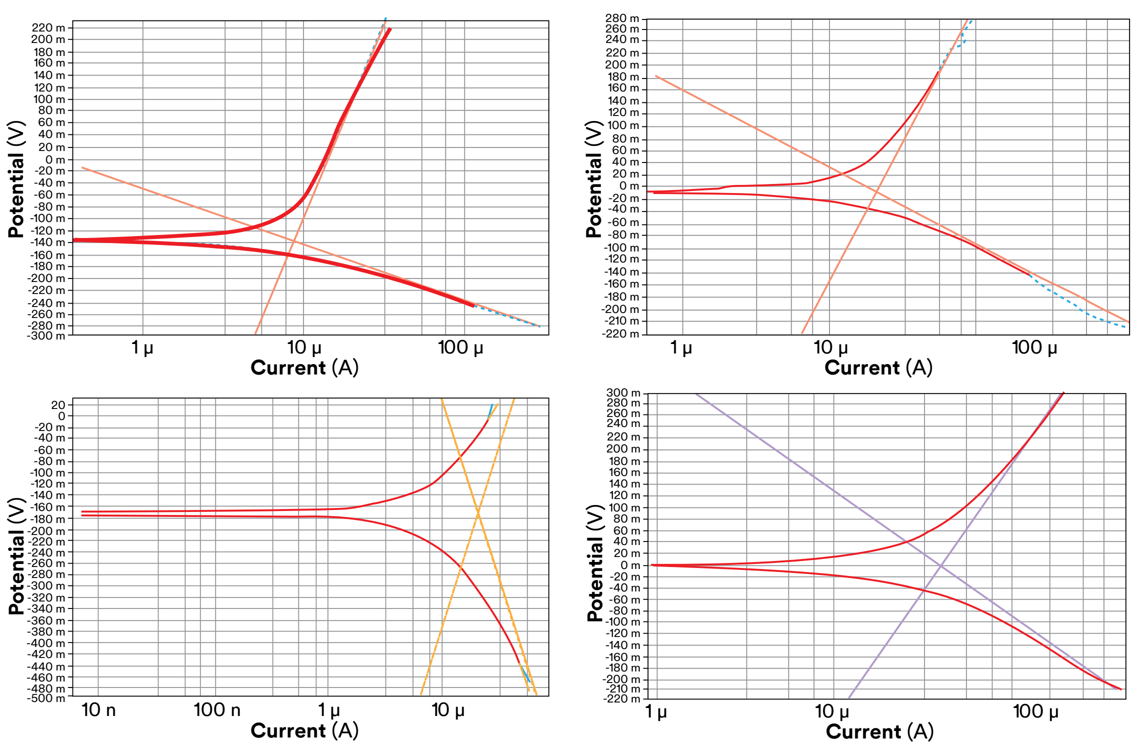

Figure 4: Tafel Plots for Compound 1 (top) and Boric Acid (bottom) at 22°C (left) and 80°C (right)

3.4 Corrosiveness

The corrosiveness of boric acid and compound 1 at 22°C and 80°C, as represented by their Tafel plots (Figure 4):

In this test, the lower the I_{corr} value the less corrosive the solution is to the stainless steel coupon working electrode.[5] The data clearly shows that 3M™ Neutron Quench compounds lead to decreased electrochemical corrosion compared to boric acid. For example, at 22°C a saturated boric acid solution has an I_{corr} of 20.387 μA while compound 1 has an I_{corr} of 8.887 μA at the same solution boron content. The reduction in corrosiveness holds at 80°C where boric acid has an I_{corr} of 39.988 μA and compound 1 and I_{corr} equal to 20.678 μA. This same corrosion testing was performed on all six compounds and all compounds display significantly less electrochemical corrosion activity (Table 4).

4 Conclusion

As the need for neutron absorption remains steady in the nuclear industry, 3M™ Neutron Quench compounds show promise to be a significantly better solution than boric acid or sodium pentaborate for emergency shutdown situations. With boron content up to 80% by weight these compounds can have almost five times more boron than boric acid and sodium pentaborate. In addition to the inherent elevated boron content, the solubility of these compounds greatly surpasses that of boric acid. This combination of characteristics results in boron concentrations that are more than 30 times that of saturated boric acid solutions, even when natural isotopic abundance boron is used. These characteristics could decrease the total amount of solution (i.e. volume) needed in an emergency situation. In addition, the pH of these compounds is neutral and the electrochemical corrosion rate has been shown to be lower than that of boric acid at both 22°C and 80°C. Further testing is underway to gain understanding of how 3M™ Neutron Quench compounds behave under emergency conditions and during long term storage as solids and in aqueous solution.

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