ARSENIC REMOVAL FROM GEOTHERMAL BORE WATER: THE EFFECT OF DISSOLVED SILICA

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SUMMARY - Arsenic adsorption onto a hydrous ferric oxide (HFO) floc is a viable option for the removal of arsenic (As) from geothermal bore waters. However, the degree of As(III) and As(V) adsorption from bore water is considerably less than that from a 0.1m $NaNO_3$ electrolyte, or than that predicted using equilibrium surface complexation constants and the geochemical speciation model, MINTEQA2. By determining the effect of individual bore water components on the adsorption of As(III) and As(V) from 0.1m $NaNO_3$, mono-silicic acid (H_4SiO_4) was identified as the main component inhibiting As adsorption. Mono-silicic acid is adsorbed onto the HFO surface when the H_4SiO_4/Fe ratio of the solid is below ca. 0.2, and polymerised on the surface at higher H_4SiO_4/Fe ratios. Both of these processes appear to inhibit As adsorption from bore water. By altering the MINTEQA2 data base to include a surface complexation constant for H_4SiO_4 adsorption onto HFO, prediction accuracy is improved. However, MINTEQA2 continues to overestimate the degree of As(III) adsorption, and of As(V) adsorption at pH > 8. This is considered to reflect the effect of H_4SiO_4 polymerisation on the HFO surface, a process which is not taken into account by the speciation model.

1.0 INTRODUCTION

In 1993 tlie World Health Organisation (WHO) decreased the guideline for arsenic (As) in drinking water from 50 μgL^{-1} to a provisional value of 10 μgL^{-1} (WHO 1993). Arsenic concentrations in New Zealand's Waikato River typically vary between 10 and 80 μgL^{-1} and several drinking water supplies that derive water from this river border on, or exceed, the revised As guideline (Davies et al. 1994). The largest source of As entering the Waikato River is tlie Wairakei Geothermal Power Station's discharge of spent bore water containing approximately 4,000 μgL^{-1} As (Aggett and Aspell 1978). Discharge options that avoid or mitigate this As contamination are currently being investigated.

Flocculation with HFO is an effective treatment process for the adsorptive removal of As from waste water, although the efficiency of As adsorption is dependent on variables such as pH and As oxidation state (Peng and Di 1994). For example, in oxygen-rich waters the predominant As species are the As(V) oxy-anions of arsenic acid (H_3AsO_4; $pK_{a1,2\&3}$ = 2.2, 6.9 and 11.5 respectively), which adsorb inost efficiently at low pH. In oxygendeficient waters, such as fresh geothermal bore water, the predominant As species is the neutral As(III) arsenious acid (H_3AsO_3; pK_a = 9.29), and adsorption is less dependent on pH (Pierce and Moore 1982). Other variables affecting As removal efficiencies include the As/Fe ratio, ionic strengtli, and the presence of coinpeting ions in solution.

A pilot scale As remuval plant has been constructed at the Wairakei Geothermal Power Station to treat spent bore water by ferric flocculation. However, the HFO adsoxption of As(III) and As(V) from Wairakei geothermal bore water has been shown to be less efficient than expected when compared to adsorption from a 0.1m $NaNO_3$ electrolyte solution (Webster and Webster 1995). Furthermore, the observed inhibition of As adsorption from bore water was not predicted by the MINTEQA2 geochemical speciation model compiled by Allison et al. (1991: MINTEQA2 calculates the degree of metal adsorption using a diffuse layer adsoxption model and experimentally-derived surface complexation constants). In fact, significant enhancement of As(V) adsorption was predicted above pH 8 by MINTEQA2, but inhibition was *observed.* One or more of the bore water components inhibited As adsorption onto HFO, and the mechanism appeared to involve solution or surface reactions which were not included in MINTEQA2's thermodynamic data base. This paper reports the results of experiments undertaken to determine the effect of individual bore water components on the HFO adsorption of As(III) and As(V) from 0.1m $NaNO_3$. Mechanisms for the inhibition of As adsorption from geothermal bore water, and the ability of MINTEQA2 to model this system, are examined.

2.0 METHODS

The HFO suspension was synthesised by rapidly raising the pH of a 0.1m $NaNO_3$ solution containing 1×10^{-3}m $Fe(NO_3)_3 \cdot 9H_2O$ from 2.0 to 7.0 and ageing tlie resulting suspension for 24 hours prior to adsoxption experiments. For adsorption experiments in Wairakei bore water the 0.1m $NaNO_3$ solution was removed from above the settled HFO floc and replaced with bore water taken from Flash Plant No. 10 at the Wairakei Geothermal Power Station. Bore water for As(III) adsorption experiments was used

between 1 and 3 weeks after sampling, during which time the As remained stable as As(III). For As(V) adsorption experiments 5 mL of 30% H_2O_2 were added per 1L of bore water to oxidise the As(III) to As(V). Although water treatment involves HFO precipitation *in situ*, a preformed and aged HFO was used in this work as the surface properties have been well characterised. The removal of As with preformed HFO and *in situ* HFO precipitation involve the same adsorption process (Fuller et al. 1993).

Adsorption experiments using synthetic solutions containing individual bore water components were prepared using the desired mount of As (5.3×10^{-5}m) and adding one, or more, bore water component(s) to the HFO suspension in 0.1m $NaNO_3$. Arsenic adsorption fiom 0.1m $NaNO_3$ was measured in the presence of the following bore water components: Cl^- (6.2×10^{-2}m); SO_4^{2-} (4.3×10^{-3}m); K^+ (5.3×10^{-3}m); Ca^{2+} (2.6×10^{-4}m); H_3BO_3 (2.7×10^{-3}m); CO_3^{2-}/HCO_3^- (1.1×10^{-3}m); and H_4SiO_4 (1.8×10^{-3}m or 2.0×10^{-3}m). The concentrations of components used were those of Wairakei bore water as given in Ellis and Mahon (1977). Ionic species were added as the Na^+ or NO_3^- salts, H_3BO_3 was added directly and H_4SiO_4 was added as a sodium silicate solution.

Initial experiments were performed in a 1L 3 neck glass vessel on a magnetic stirrer at room temperature. The suspension pH was raised to 12 and then lowered sequentially in steps of 1-1.5 pH units with HNO_3. The pH was remeasured and the suspension sampled 30 minutes after each pH adjustment. The sample was filtered (0.45μm membrane) and the filtrate analysed for As. A 30 minute reaction time was chosen because it was similar to the time between floc formation and phase separation at the Wairakei pilot plant. Subsequent experiments determined equilibrium As adsorption fiom both bore water and 0.1m $NaNO_3$, with and without H_4SiO_4. The suspension was prepared as described above and experiments were perfomed in HDPE bottles agitated on a side to side shaker at 25°C.

Samples were analysed for total inorganic As by Hydride Generation Atomic Adsorption Spectrophotometry (HGAAS) as described by Aggett and Aspell (1976). Selected samples were also analysed for As(III) by HGAAS on a sample buffered at pH 6 with 1M citrate buffer. This demonshated that As(III) oxidation was not occurring during the As(III) experiments. Total silica was measured by AAS using a N_2O/C_2H_2 flame after adding 1mL of 1m NaOH and 10,000ppm EDTA per 10 mL sample. Molybdate-reactive silica was measured spectroscopically by the method of Iler (1979). Colour development in both bore water and sodium silicate solutions was complete within 90s and therefore all molybdate reactive silica was considered to be mono-silicic acid (H_4SiO_4).

3.0 RESULTS

The results fiom the 30 minute sequential experiments are described in this section, whereas the results for equilibrium experiments are given in Section 4.0 in relation to modelling As adsorption. The HFO adsorption of As(III) and As(V) from 0.1m $NaNO_3$ was not significantly affected by Cl^-, H_3BO_3, K^+, or CO_3^{2-}/HCO_3^- at concentrations typical of Wairakei bore water. Sulfate inhibited the adsorption of As(III) by 5 to 10% between pH 5 and 3, but did not significantly affect As(V) adsorption. The bore water components having the most significant effect on As adsorption were H_4SiO_4 and Ca^{2+}.

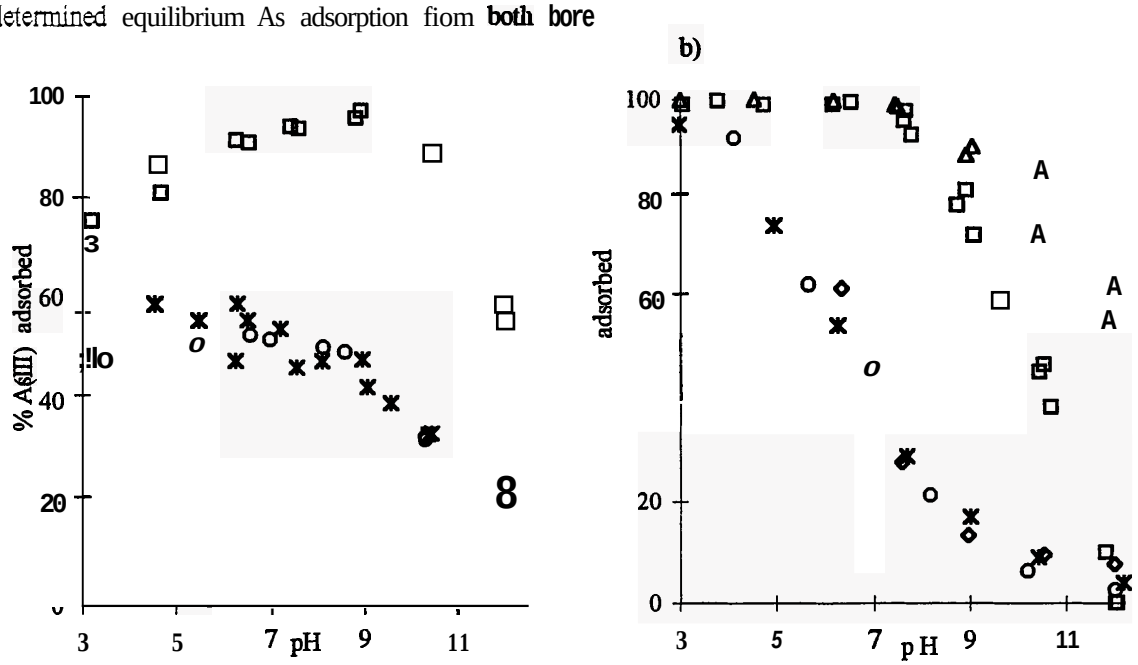

Figure 1. The adsorption of As(III) (a) and As(V) (b) from bore water compared to adsorption from 0.1m $NaNO_3$, and from 0.1m $NaNO_3$ with H_4SiO_4 and/or Ca^{2+}. Adsorption curves shown are as follows: 5.3×10^{-5} m As from 0.1m $NaNO_3$ (□), 5.3×10^{-5} m As from 0.1m $NaNO_3$ with 2.0×10^{-3} m H_4SiO_4 (o), 4.7×10^{-5} m As from bore water (*), 5.3×10^{-5} m As(V) from 0.1m $NaNO_3$ with 2.6×10^{-4} m Ca^{2+}(Δ), 5.3×10^{-5} m As(V) from 0.1m $NaNO_3$ with 2.0×10^{-3} m H_4SiO_4 and 2.6×10^{-4} m Ca^{2+}(◊).

When Wairakei geothermal bore water is cooled, H_4SiO_4 polymerises to form an amorphous silica colloid ($SiO_{2(am)}$) which has a solubility of 1.94×10^{-3}m at 25°C. After storing bore water at room temperature for 1 week the H_4SiO_4 concentration was stable at 2.0×10^{-3}m, compared to the total SiO_2 concentration of 8.3×10^{-3}m. In contrast, sodium silicate added to 0.1m $NaNO_3$ at the start of As adsorption experiments was initially all present as H_4SiO_4. The adsorption of As(III) and As(V) fiom 0.1m $NaNO_3$ to which 2.0×10^{-3}m sodium silicate was added was almost identical to that observed from bore water (Figures 1(a) and 1(b)). In addition to the effect of H_4SiO_4, the adsorption of As(V) from 0.1m $NaNO_3$ at pH>8 was significantly enhanced in the presence of 2.6×10^{-4}m Ca^{2+}, although As(V) precipitation or co-precipitation with Ca^{2+} minerals was not observed in the absence of HFO. The Ca^{2+} enhancement of As(V) adsorption was not observed from bore water or from 0.1m $NaNO_3$ with 2.6×10^{-4}m Ca^{2+} and 2.0×10^{-3}m H_4SiO_4.

4.0 DISCUSSION

4.1 Modelling Adsorption

The surface complexation model considers adsorption as surface complex formation between sorbing species and hydroxylated surface metal sites, $\equiv FeOH^0$ (Dzombak and Morel 1990). Surface sites are considered to be amphoteric (Equations 1 and 2) and cation adsorption to be co-ordination by ionised surface hydroxyl groups (Equation 3). Oxy-anion and oxy-acid adsorption is considered as the exchange of surface hydroxyl groups with the sorbing species (Equations 4 and 5). The degree of protonation of these surface species is dependent on pH and is considered to parallel that of solution species. The extent of adsorption reactions depends upon the chemical free energy of adsorption, considered to be an intrinsic constant K^{INT}, and the coulombic free energy of adsorption, a variable term dependent on surface charge.

$$\equiv FeOH_2^+ \Leftrightarrow \equiv FeOH^0 + H^+ \quad (1)$$

$$\equiv FeOH^0 \Leftrightarrow \equiv FeO^- + H^+ \quad (2)$$

$$\equiv FeOH^0 + Ca^{2+} \Leftrightarrow \equiv FeOCa^+ + H^+ \quad (3)$$

$$\equiv FeOH^0 + H_3AsO_3 \Leftrightarrow \equiv FeH_2AsO_3^0 + H_2O \quad (4)$$

$$\equiv FeOH^0 + H_3AsO_4 \Leftrightarrow \equiv FeHAsO_4^- + H_2O + H^+ \quad (5)$$

4.2 Adsorption of H_4SiO_4

The MINTEQA2 HFO adsorption data base did not include H_4SiO_4 binding constants due to the absence of data at the time of compilation. Therefore MINTEQA2 was not able to predict inhibition of As adsorption from bore water. The interaction between H_4SiO_4 and the HFO surface is considered to involve two processes depending on the adsorption density Γ_{H4SiO4} (ie. the solid phase Si/Fe ratio; Herbillon and Tran Vinh An 1969). The number of HFO surface sites available for adsorption is considered to be 0.2 mol per mol Fe, and when Γ_{H4SiO4} is less than ca. 0.2, H_4SiO_4 is considered to adsorb at HFO surface sites in the same way as other oxy-acids, for example H_3AsO_3 in Eq. 4. This adsorption has been successfully described by the diffuse layer model for Γ_{H4SiO4} of ca. 0.05, between pH 4 and 6, with an intrinsic adsorption constant $\log K_1^{INT}{}_{H4SiO4}$ of 3.62 (Hansen et al. 1994).

At Γ_{H4SiO4} greater than ca. 0.2, H_4SiO_4 is considered to polymerise as a separate silica phase on the HFO surface. This polymerisation occurs at H_4SiO_4 concentrations below saturation with respect to a $SiO_{2(am)}$ bulk phase and has been identified by IR and Differential Thermal Analysis of HFO exposed to H_4SiO_4 (Herbillon and Tran Vinh An 1969). For example, the temperature of crystallisation to haematite increased from 300 to 800°C as the Si/Fe ratio increased fiom 0 to 0.13. However, above this ratio additional Si did not affect the temperature of haematite crystallisation and characteristic silica Si-O stretching bands in the IR spectra began to appear. The polymerisation of silica on the HFO surface decreases the HFO pH point of zero charge (PZC) from 8.0 in the absence of H_4SiO_4 to ca. 4.0 with a Γ_{H4SiO4} of 0.35 (Anderson and Benjamin 1985). The PZC of pure amorphous silica is approximately 2.0 (Iler 1979).

The H_4SiO_4 adsorption constant derived by Hansen et al. (1994) was added to the MINTEQA2 data base. The predicted and observed equilibrium adsorption of 1.8×10^{-3}m H_4SiO_4 onto HFO, from 0.1m $NaNO_3$ (without As) is shown in Figure 2. Adsorption of H_4SiO_4 was slow and required between 1 and 6 days to reach equilibrium. The observed H_4SiO_4 adsorption exceeded predicted adsorption, and the Γ_{H4SiO4} ranged up to 0.45. This implied that significant H_4SiO_4 polymerisation had occurred at the HFO surface and, as this polymerisation is not considered by the model, MINTEQA2 could not predict this behaviour.

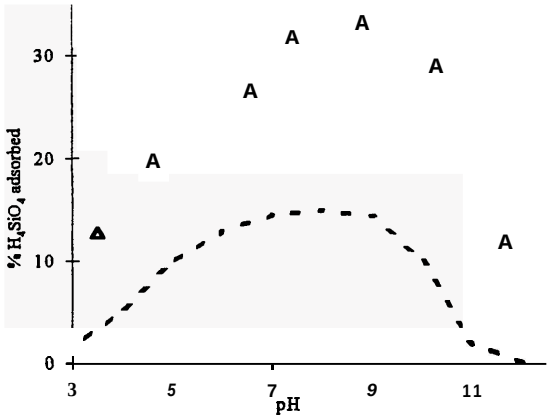

Figure 2. Comparison of the observed experimental and MINTEQA2 predicted H_4SiO_4 adsorption from 0.1m $NaNO_3$. Adsorption curves shown are MINTEQA2 predictions (. . .), and experimentally determined adsorption of 1.8×10^{-3}m H_4SiO_4 (A).

4.3 Arsenic Adsorption in the Presence of H_4SiO_4

The predicted and observed equilibrium adsorption of As(III) and As(V) fiom bore water, and fiom 0.1m $NaNO_3$ with and without 2.0×10^{-3}m H_4SiO_4, are given in Figures 3(a) and (b) respectively. Adsorption of As(III) reached equilibrium within ca. 24 hours, whereas adsorption of As(V) was more rapid, especially at low pH where equilibrium was reached in less than 1 hr, even in tlie presence of H_4SiO_4. In view of tlie slow adsorption kinetics for H_4SiO_4 adsorption, the reason for this is unclear. The extent of As(III) and As(V) adsorption from bore water was almost identical to adsorption from 0.1m $NaNO_3$ with 1.8×10^{-3}m H_4SiO_4.

Without alteration to the HFO adsorption data base, MINTEQA2 predicts As(III) adsorption fiom bore water to be similar to that fiom 0.1m $NaNO_3$. Even when $logK_1^{INT}{}_{H_4SiO_4}$ is included in MINTEQA2 the predicted As(III) adsorption from bore water is only ca. 10% less than that from 0.1m $NaNO_3$, whereas the observed inhibition was between 30 and 40%. MINTEQA2's underestimation of the inhibitory effect of H_4SiO_4 on As(III) adsorption may again be due to its failure to take account of surface H_4SiO_4 polymerisation, which may affect As(III) adsorption.

MINTEQA2 under-predicted As(V) adsorption fiom 0.1m $NaNO_3$, and predicted enhanced As(V) adsorption fiom bore water at pH>8. This predicted enhancement of As(V) adsoxption was due to the effect of Ca^{2+} adsorption on the modelled HFO surface charge.

From Figure 1(b) it can be seen that Ca^{2+} did enhance As(V) adsorption at pH>8, but not from bore water nor from 0.1m $NaNO_3$ with 2.6×10^{-4}m Ca^{2+} which also contained 2.0×10^{-3}m H_4SiO_4. When $logK_1^{INT}{}_{H_4SiO_4}$ was added to MINTEQA2 the agreement of predicted and observed As(V) adsorption fiom bore water at pH<8 was good, but possibly coincidental, due to the underestimation of both As(V) adsorption from 0.1m $NaNO_3$ and the effect of H_4SiO_4 on As(V) adsorption. The predicted As(V) adsorption fiom bore water was still enhanced at pH>8 when MINTEQA2 included $logK_1^{INT}{}_{H_4SiO_4}$, though this was not observed.

There are several possible reasons why tlie Ca^{2+} enhancement of As(V) adsorption was not observed from system with H_4SiO_4. In bore water both the precipitation of $CaCO_3$ at pH>10 and/or tlie interaction between Ca^{2+} and colloidal silica may prevent Ca^{2+} enhancing As(V) adsorption. However, neither a $CaCO_3$ precipitate nor colloidal silica were present in the 0.1m $NaNO_3$ solution with Ca^{2+} and H_4SiO_4 (Figure lb). In this system the silica phase formed by the polymerisation of H_4SiO_4 on the HFO surface, being more negatively charged than the HFO, could either offset the effect that Ca^{2+} adsorption had on HFO surface charge and/or attract Ca^{2+} more strongly than the HFO phase. In addition, although no precipitation was observed fiom 0.1m $NaNO_3$ solutions with Ca^{2+} and H_4SiO_4 in the absence of HFO, there are several calcium silicate minerals that may form as an indiscernible colloid which could have removed Ca^{2+} fiom this solution.

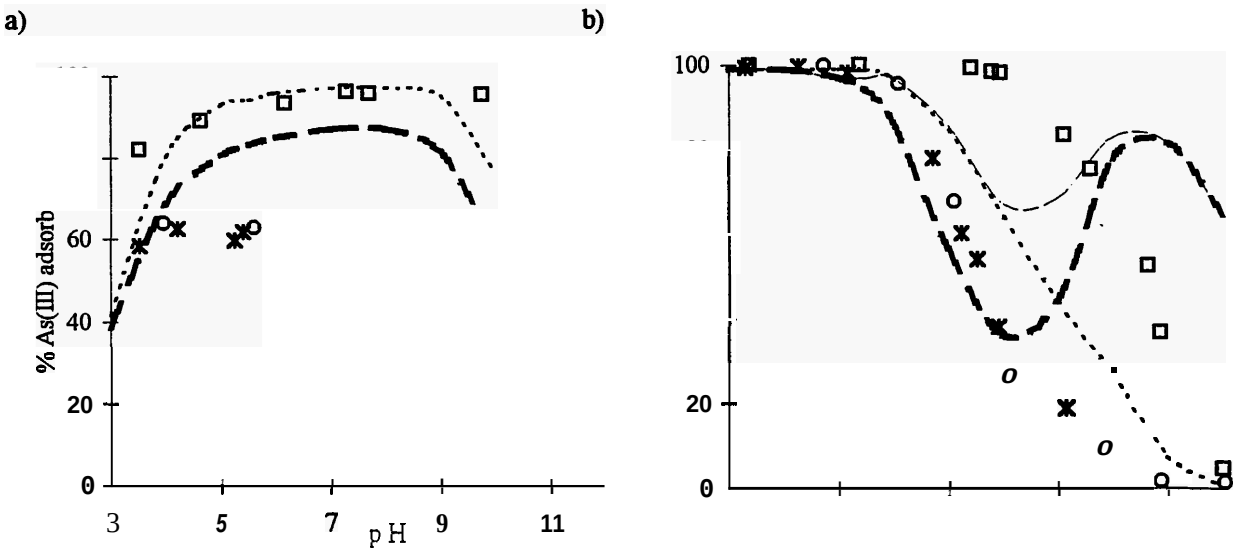

Figure 3. Comparison of the experimental and MINTEQA2 predicted As(III) (a) and As(V) (b) adsorption fiom bore water, and fiom 0.1m $NaNO_3$ with and without H_4SiO_4. Adsorption curves are shown as follows; 5.3×10^{-5}m As from 0.1m $NaNO_3$ (O), 5.3×10^{-5}m As from 0.1m NaNQ with 2.0×10^{-3}m H_4SiO_4(o), 4.7×10^{-5}m As from bore water (*), MINTEQA2 predicted adsorption for 5.3×10^{-5}m As from 0.1m $NaNO_3$ (...), MINTEQA2 (without K_1 for H_4SiO_4 adsorption) predicted adsorption for 4.7×10^{-5}m As(V) from bore water (— —), and MINTEQA2 (altered to include a K_1 for H_4SiO_4 adsorption) predicted adsoxption for 4.7×10^{-5}m As from bore water (– –).

5.0 CONCLUSION

Flocculation with HFO can be an effective water treatment process to remove As from geothermal bore water. Because the adsorption of As(III) and As(V) from bore water is inhibited by the high concentrations of H_4SiO_4 found in bore water, efficient As removal can only be achieved at low pH and with tlie As(V) oxidation state. The bore water H_4SiO_4 appears to inhibit As adsorption by competition for adsorption sites and by polymerising on the HFO surface. The ability of MINTEQA2 to predict As adsorption from bore water is improved by including tlie K_1 for H_4SiO_4 adsorption derived by Hansen et al. (1994). However, tlie effect of H_4SiO_4 polymerisation is not considered by MINTEQA2, and the $Ca^{2+}/H_4SiO_4/HFO$ interactions are therefore incorrectly modelled.

6.0 ACKNOWLEDGMENTS

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