

ASSESSMENT OF FLUID ACIDITY IN ALTO PEAK AND MAHANAGDONG GEOTHERMAL FIELDS, LEYTE, PHILIPPINES

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Abstract

Development of Alto Peak and Mahanagdong geothermal fields in Leyte has been constrained by the presence of acid fluids. These acid Cl-SO₄ waters are of deep origin. Their characteristics are studied to identify the possible source of acidity. In Alto Peak, the acid fluids have high gas levels and sulfate concentrations (>1000 mg/kg) and contain excess Cl. The acid waters are produced in wells drilled at the core of the system where temperature exceeds 320°C. These fluids are interpreted to contain fresh supply of magmatic species of HCl and H₂SO₄. In Mahanagdong, the acid waters are confined north of the postulated upflow region. Four wells discharged acid waters with pH of 2.9-5.9 and SO₄ concentration of 70-900 mg/kg. Stable isotope data showed that these waters are depleted of heavy isotopes compared with the neutral-pH waters in the field. Moreover, the sulfur isotope suggest equilibration temperature of 270°C which does not reflect active magmatic environment. Other chemical evidences also do not point to a definite magmatic origin of acidity. Corrosion experiments and actual well blowout proved that the acid waters from both fields are very corrosive and therefore unsuitable for production.

1.0 INTRODUCTION

Mahanagdong geothermal field is presently being developed for a large scale power generation slated for the Leyte-Luzon grid. Its development is being hampered by the presence of acid fluid **within** the high temperature region. Similar constraint is found in the development of the Alto Peak geothermal field, located southeast of Mahanagdong. Both geothermal fields are located in a volcanic zone and are situated within the proximity of a collapse structure. Alto Peak hosts a very impressive solfatara in its crater region. On the other **hand**, only cold to warm acid-sulfate **springs** and fumaroles are found in the flanks of Mahanagdong. Both geothermal fields lack neutral-pH chloride **springs** in their respective outflow region.

This paper **aims** to **study** the chemical characteristics of the acid fluids in Alto Peak and Mahanagdong fields. The similarities and differences of the fluid chemistry are analysed in view of understanding the fluid genesis. This paper also aims to **assess** the commercial potential of the fluids.

2.0 CHEMICAL AND ISOTOPIC CHARACTERISTICS

2.1 Chemistry of the Water Phase

Table 1 of the attached **Appendix** shows the representative water chemistry of the acid wells in Mahanagdong and Alto Peak geothermal fields. Mahanagdong waters are **classified as** acid-chloride-sulfate with pH of 2.2-5.9 at atmospheric condition (Fig. 2). The reservoir sulfate has a wide range in concentration at 20-350 **mg/kg** (Parrilla et al., 1995). In MG-15D, the waters were noted to have SO₄ of less than 100 mg/kg but with pH level of about 3.6-5.0.

The other chemical signatures of the acid fluids in Mahanagdong include elevated levels of magnesium and **iron** at the weirbox ranging from 13-31 and 50-230 mg/kg, respectively. Part of the Fe concentration though may have come from the casing due to corrosion. The reservoir chloride concentrations are likewise comparable to the neutral wells **within** the upflow region at 2510-4970 mg/kg suggesting that the acid fluids are coming from a deep source and not from shallow **steam-heated** reservoir.

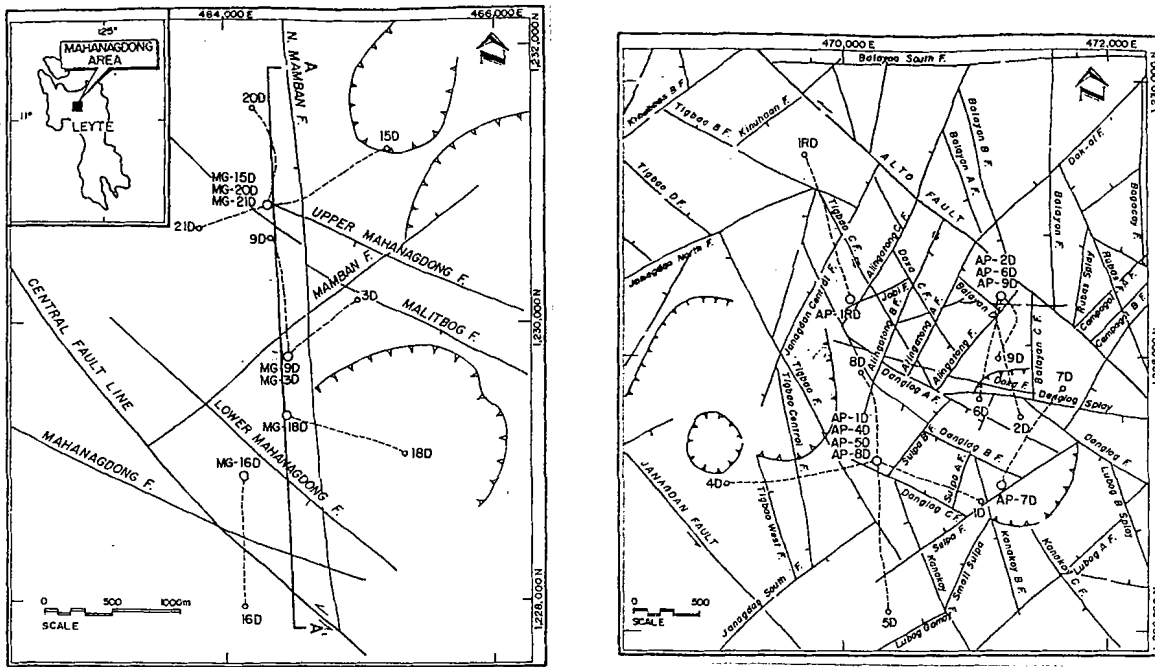


Fig.1: Location map of Mahanagdong and Alto Peak fields, and the welltracks of selected wells.

The increase in Cl/B ratio is highly noticeable from the neutral-pH reservoir at 22-24 to 70-95 in the acid reservoir. This increase is attributed to the decrease in relative concentration of Boron possibly due to the contribution of magmatic fluids depleted in Boron.

The Alto Peak fluids are likewise classified as acid Cl-SO₄ waters with pH at atmospheric condition measured at 2.1-5.0. Comparing the milliequivalents of Cl⁻ against Na⁺+K⁺ showed higher "excess" chloride in the Alto Peak acid waters compared to that of MG-9D in Mahanagdong (Fig.3). The excess Cl in Alto Peak of around 10⁻² meq/liter roughly translates to a pH of 2.0 which is the measured pH of the waters. This suggests the presence of HCl in the waters. A neutral-pH dilute chloride-sulfate-bicarbonate pool is located among the low chloride steam heated groundwaters in the Danglog solfatara. The chloride of this spring could come from volcanic gases containing HCl which has undergone neutralization. The neutral pH could also be due to the buffering of NH₄ which is noted to be high in this area.

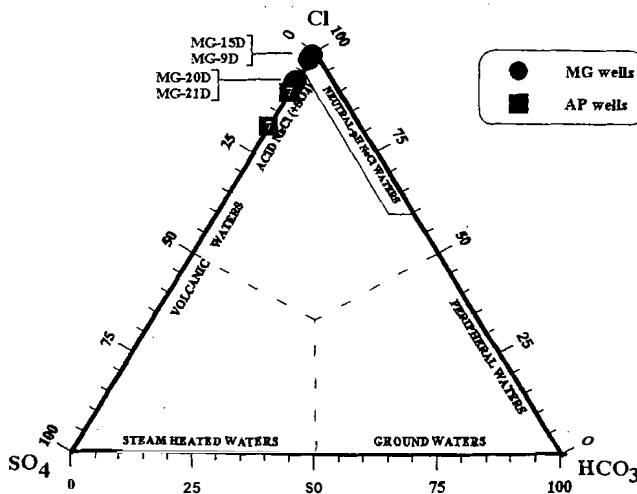


Fig.2: The Cl-SO₄-HCO₃ ternary plot of the acid waters from Alto Peak (AP) and Mahanagdong (MG) fields

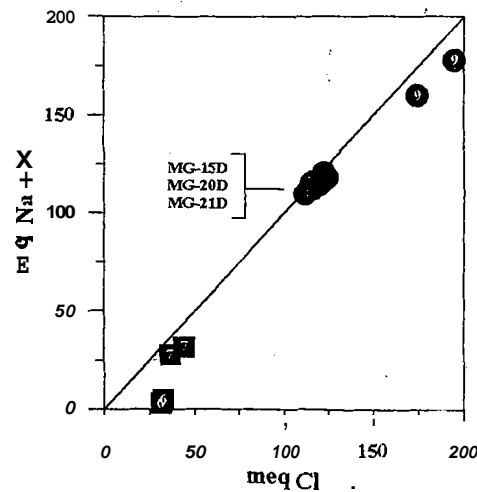


Fig. 3: Plot of Cl vs. [Na+K] (in meq) in the waters of Alto Peak (AP) and Mahanagdong (MG) acid wells.

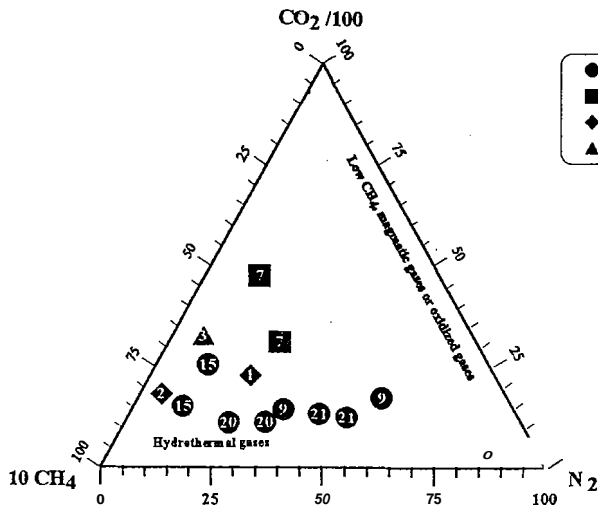


Fig. 4: The CO₂-CH₄-N₂ ternary plot of the gases in Alto Peak (AP) and Mahanagdong (MG).

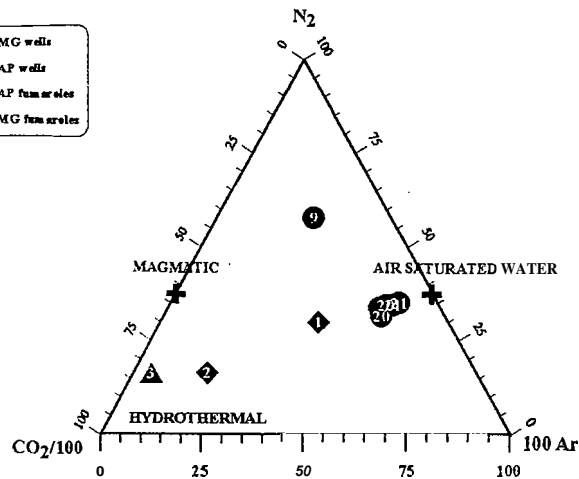


Fig. 5: The N₂-CO₂-Ar ternary plot of the gases in Alto Peak (AP) and Mahanagdong (MG).

2.2 Chemistry of the Gas Phase

The gases consist mainly of CO₂ at 95% of the total composition. The H₂S levels in both fields (24-405 mmoles/100 moles steam) are higher than the typical neutral-pH wells (<25 mmoles/100 moles steam). Both fields have appreciable amount of CH₄ with CH₄/CO₂ ratio >0.0001 indicating predominance of hydrothermal environment. The Mahanagdong fluids have higher CH₄/CO₂ ratio at 0.001-0.004 compared to the Alto Peak acid fluids at 0.0004, suggesting that the latter still has the signature of the magmatic gases. This is illustrated by the CO₂-CH₄-N₂ ternary diagram (Fig. 4) which shows that the Mahanagdong acid fluids are nearer to the CH₄ apex indicating their likely hydrothermal environment compared to the Alto Peak fluids.

In N₂-CO₂-Ar ternary diagram (Fig. 5), MG-9D has no magmatic affinity because its data point plotted away from the magmatic corner. The other low-pH Mahanagdong wells clustered near the air saturated groundwater region. These suggest that there is no active magmatic contributions to the acid fluids in Mahanagdong. The fluids may have already reacted with the reservoir rocks that part of the signature of magmatic gases have already been erased. On the other hand, the MG-21D data can also be due to the inflow of neutral-pH fluids in the bottom permeable zone. The data plotted are representative of each wells as presented in Table 2 of the attached Appendix.

2.3 Stable Isotope Chemistry

Alto Peak waters were found to be more enriched with heavy isotopes compared to Mahanagdong field. The magmatic component of Alto Peak waters was calculated to be around 65% (Salonga, 1996). In Mahanagdong, the stable isotope composition of the acid waters was found to be similar to that of the neutral-pH waters (Salonga and Siega, 1996). In fact, the most isotopically enriched waters are those from the neutral wells near the upflow zone and not the acid wells. The magmatic component of waters in Mahanagdong is only about 32% (Salonga and Siega, 1996). Moreover, the $\delta^{18}\text{O}_{\text{H}_2\text{O}}-\delta^{18}\text{O}_{\text{SO}_4}$ geothermometer showed that these waters have equilibrated at 280°C which is also the measured temperature in the area.

3.0 FLUID-MINERAL EQUILIBRIA

3.1 Dissolved Sulfur Species

Figure 6 shows the trend of the different dissolved sulfur species in waters at different boiling temperatures. The values in the graph were calculated using WATCH speciation program of Arnorsson (1990). In the plot, dissolved H_2S in all the wells decrease from 10^{-2} moles/liter (M) to about 10^{-5} M with decline in temperature. This is possibly due to the partitioning of H_2S to gaseous phase upon boiling. Similarly, the HS^- level in the waters decrease upon boiling indicating that the acidity of the waters are not due to Qs association of H_2S and HS^- .

The HSO_4^- levels in Mahanagdong wells decrease from 10^{-3} M to about 10^{-4} M upon boiling. This is paralleled by the increase in SO_4^{2-} from 10^{-4} M to about 10^{-3} M. These trends indicate that HSO_4^- tend to dissociate to SO_4^{2-} and H^+ upon boiling and thus contributing to the acidity of the waters.

In Alto Peak, both the HSO_4^- and SO_4^{2-} levels in the waters tend to rise with boiling. This means that there is another species contributing to their increases. This is possibly the disproportionation of SO_2 gas associated with HCl emanations in magmatic systems.

3.2 Mineral Equilibria

The plots of the acid wells with respect to different secondary minerals are shown in Figures 7a to 7b. The Mahanagdong wells plotted in illite field in $\text{Log}(K/H)$ plot (Fig. 7a), in Na-montmorillonite in $\text{Log}(Na/H)$ plot (Fig. 7b), in Ca-montmorillonite in $\text{Log}(Ca/H^2)$ plot (Fig. 7c), and in chlorite in $\text{Log}(Mg/H^2)$ plot (Fig. 7d). These are the same stable minerals found in the neutral-pH wells. Therefore, the acid fluids in Mahanagdong have attained some degree of mineral equilibration. None attainment of full equilibration between the fluids and the rocks can be attributed to the weak buffering capacity of HSO_4^- as the major acid species. At reservoir temperature, HSO_4^- does not readily dissociate and therefore cannot induce water-rock reactions. However, at lower temperature, HSO_4^- readily dissociates to SO_4^{2-} and H^+ and thus causing acidity to the waters.

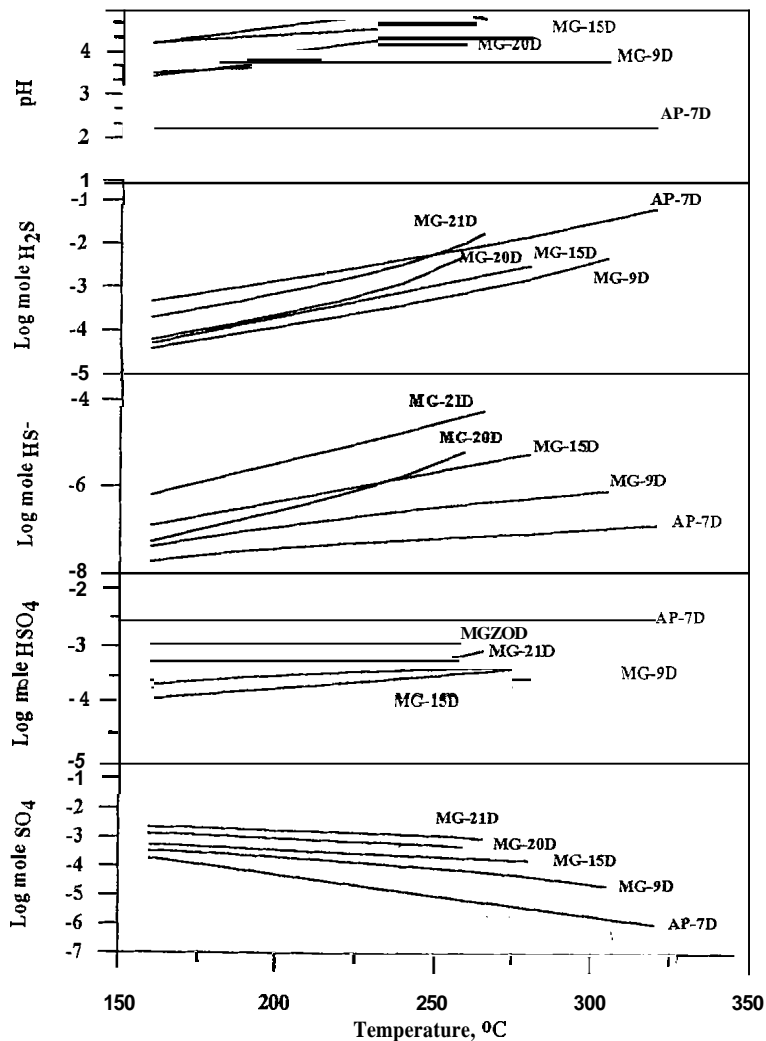


Fig. 6: Trends of dissolved sulfur species upon boiling.

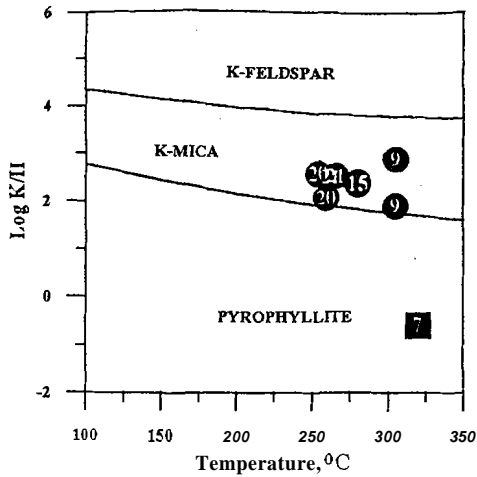


Fig. 7a: $\text{Log}(K/H)$ vs. temperature

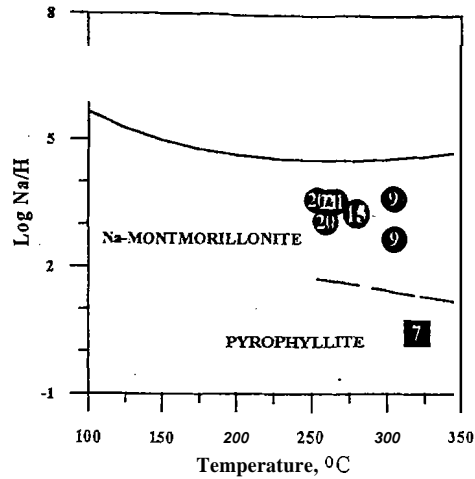


Fig. 7b: $\text{Log}(Na/H)$ vs. temperature

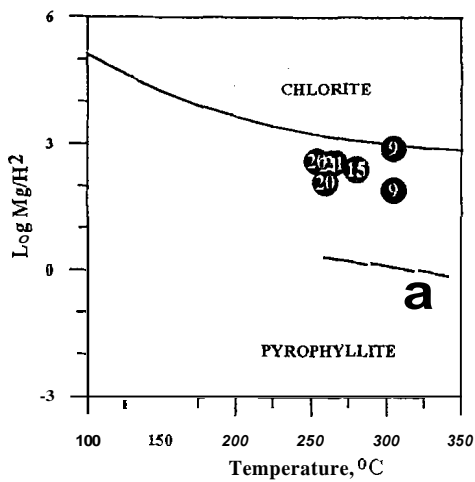
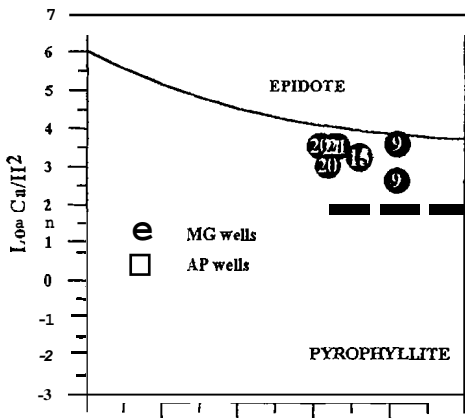


Fig. 7d: $\text{Log}(Mg/H^2)$ vs. temperature

In Alto Peak, the waters are presently **in-equilibrium** with pyrophyllite. This means that the prevailing reaction in the reservoir is rock dissolution. This is **made possible** by the strong activity of HCl as the major acid species in the waters.

4.0 THE CORROSIVE POTENTIALS OF THE FLUIDS

The acid fluids from Alto Peak are found to be **highly** corrosive compared to those **emanated** from Mahanadong. This is illustrated by the massive leakage in the wellhead assembly in well AP-6D which lead to an uncontrollable discharge. The leak developed overnight when the well was put on bleed in preparation for a long term discharge test.

The acid fluids in Mahanadong are **also highly** corrosive but of a lesser intensity. These wells were discharged for a duration **from 5 to 21 days** and inspection of the pipes showed **signs** of corrosion (Parrilla, 1996). Corrosion probes and pipe wall thinning established a corrosion rate of 0.228 **mm/day** proving that these fluids can cause rapid corrosion on carbon steel materials.

5.0 MODEL OF ACID FLUID ORIGIN

5.1 Mahanagdong

Based on the chemical characteristics, both the acid and the neutral-pH fluids in Mahanagdong field are coming from a dominantly hydrothermal system. This is reflected on the similarity in the Cl levels, in the alteration minerals, in the stable isotope composition, and in the CO_2/CH_4 gas ratios of the two types of fluids. Their differences, however, is the higher level of sulfur in the acid fluids as shown in the elevated SO_4 in the waters, the high H_2S in the gases, and the presence of abundant sulfur sublimates at the shallow part of the acid wells. There are two theories regarding the differences in the chemistry of these fluids. One is the incomplete water-rock interaction, and the other one is the contribution from magmatic sources.

Regarding the first theory, the acid fluids in Mahanagdong are confined in the northern part of the field where a natural fluid outflow did not develop owing to the poor lateral permeability. The lack in permeability restricted fluid-rock interaction which did not allow the fluids to attain full equilibration. Moreover, the major acid species in Mahanagdong fluids is HSO_4^- which, being a weak buffer at reservoir temperature, cannot initiate rock dissolution process that will effectively "cleanse" the fluids of free H^+ . However at lower temperature it dissociates to SO_4^{2-} and H^+ , and thus causing fluid acidity. Because of the low activity of acid species at reservoir conditions, the alteration minerals at depths is similar to those of the neutral-pH fluids, such as *K-mica*, and Na- and Ca- clays.

The second theory is based on the wide discrepancy of the Cl/B ratios of the two types of fluids. In the acid reservoir, the fluids are relatively depleted of B which is thought to be caused by addition of B-depleted magmatic fluids. Moreover, there are excess chloride in the waters of MG-9D by as much as 10^{-3} to 10^{-4}M which possibly reflect the presence of magmatic HCl. This theory, however, is not supported by the stable isotope composition of water and SO_4 .

5.2 Alto Peak

A magmatic-hydrothermal system can be found in the center of the Alto Peak reservoir. The acidity of the fluids discharged from wells AP-6D and AP-7D is due to emanation of magmatic volatiles from the core of Alto Peak system (Salonga, 1996). Strong evidence of the presence of magmatic fluids is the relatively higher contribution of the "andesitic waters" at 65% based on the stable isotope data (δD and $\delta^{18}\text{O}$ mixing diagram). Moreover, ionic balance between chloride and sodium + potassium showed that there is an "excess" Cl in the order of 10^{-2}M . The acid fluids are discretely channeled by structures (Danglog, Danglog Splay and Doxa-B Faults). Immediately beyond this acid channel are structures tapping neutral-pH waters. Except for AP-2D, the other neutral wells have poor permeability.

6.0 IMPLICATIONS TO DEVELOPMENT

In Alto Peak, the proximity of the acid fluids with the neutral-pH waters poses a great threat during development. Moreover, the presence of HCl acid in Alto Peak made the fluids highly corrosive both in reservoir and surface conditions. These and the poor permeability of most wells tapping neutral-pH waters does not warrant further development activities in the area.

In Mahanagdong, the acid fluids may be less corrosive compared to the Alto Peak fluids, but just the same, the fluids can cause fast and severe corrosion to the carbon steel which is presently the materials used in surface pipelines. Corrosion-resistant materials may be employed in Mahanagdong, only if proven commercially viable.

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Appendix: Water and Gas Chemistry of Acid Wells and Fumaroles (MG–Mahanagdong wells; AP–Alto Peak wells)

Table 1: Water discharge chemistry of acid wells in Mahanagdong and Alto Peak fields.

WELL	H kJ/kg	SP MPaa	pH 25°C	Na	K	Ca	Mg	Fe	Cl	F	SO ₄	SiO ₂
				mg/kg								
MG-9D	1287	0.480	3.1	3117	950	82	25	282	6175	3.1	508	910
	1450	0.858	3.4	3500	1000	133	18	64	6905	1.9	104	938
MG-15D	1403	0.795	5.0	2387	547	60	7.9	8.5	4386	1.6	62	778
	1269	1.561	3.6	2307	560	40	9.6	22	4256	1.5	88	769
MG-20D	1088	0.572	3.6	2383	450	37	18	62	4076	1.5	327	612
	1050	0.392	2.9	2650	500	30	17	58	4114	1.8	348	766
MG-21D	1139	0.542	3.3	2287	400	40	13	47	3954	2.8	333	679
	1181	0.642	3.3	2492	467	20	15	58	4322	2.9	358	696
AP-6D	1400	0.093	2.3	64	10	333	92	273	1105	2.1	195	258
	1400	0.093	4.6	99	20	513	120	525	1148	1.5	399	563
AP-7D	1254	0.600	2.1	587	90	40	15	101	1289	0.8	146	615
	1540	1.450	2.1	675	100	70	31	355	1567	0.9	360	632

Table 2: Gas discharge chemistry of acid wells in Mahanagdong and Alto Peak fields.

WELL	H kJ/kg	SP MPaa	CO ₂	H ₂ S	NH ₃	He	H ₂	Ar	N ₂	CH ₄
			mmoles/100moles steam							
MG-9D	1287	0.480	400	24.3	0.24	n.a.	0.088	0.051	12.667	0.954
	1450	0.856	580	29.1	0.10	0.003	1.226	0.206	13.820	2.083
MG-15D	1403	0.795	997	34.6	0.43	0.003	0.465	n.a.	4.522	2.474
	1269	1.561	882	42.4	0.21	n.a.	2.306	n.a.	6.508	4.325
MG-20D	1088	0.572	825	40.7	0.13	0.006	3.205	0.347	23.216	4.199
	1050	0.392	739	40.6	0.04	0.006	5.880	0.259	15.789	4.401
MG-21D	1179	0.512	1016	128	0.19	0.003	5.202	0.623	40.145	3.113
	1177	0.612	872	133	0.20	0.005	5.376	0.433	28.097	2.888
AP-7D	1254	0.605	1638	238	0.06	n.a.	9.967	n.a.	13.036	2.322
	1540	1.450	2817	405	0.03	n.a.	14.954	n.a.	7.178	2.394

Table 3: Gas chemistry of fumaroles in Mahanagdong and Alto Peak fields.

Fumaroles	Temp (°C)	CO ₂	H ₂ S	NH ₃	He	H ₂	Ar	N ₂	CH ₄
		mmoles							
Mahanagdong	98	9591	59.39	n.a.	n.a.	4.786	0.052	20.65	17.87
Danglog		1667	61.2	n.a.	n.a.	67.03	0.205	16.39	4.01
Danglog		4583	154.03	n.a.	n.a.	99.59	0.128	12.05	19.35

Note: n.a. means data not available