FLUID AND MINERAL EQUILIBRIA IN ACID $NaCl(+SO_4)$ RESERVOIR: THE CASE OF SANDAWA COLLAPSE, MT. APO HYDROTHERMAL SYSTEM

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Abstract

Three types offluids reside inside the Sandawa Collapse, namely, the acid $NaCl(+SO_4)$, *the neutral-pH* $NaCl$ *brine and the acid* SO_4*-Cl fluids. The first type offluids occupies the central sector* **of** *Sandmva Collapse marked by wells KN-1D, KN-2D and KN-3. It contains high amounts* of *dissolved SO, and* HSO_4, *both* **of** *which are products* of *sulfuric acid dissociation, and its major dissolved salt is NaCl. At reservoir conditions, sulfuric acid dissociates to* HSO_4 *and* H^+ *– with only a mole* H^+ *liberated, thejluids have an apparent neutral reservoir pH. The reservoirfluids are in-equilibrium with K-mica, and this is confirmed by the presence* **of** *abundant secondary biotite in the rock cuttings. Upon boiling to lower temperature, sulfuric acid dissociates to SO, and* $2H^+$ *thus shifting the fluid pH to acidic level. The fluids containing more than 500 mg/kg SO„ (KN-1D) became in-equilibrium with kaolinite upon boiling, but those haying less than* **500** *mgkg* SO_{4res} *remained in-equilibrium with K-mica. Neutralisation processes through deposition* **of** *sulfur-bearing minerals like pyrite, chalcopyrite, bornite and anhydrite effectively cleanse the acid* $NaCl(+SO_4)$ *fluids* of *dissolved sulfur species. From originally acidfluids, neutralisationprocesses transform the acid* $NaCl(+SO_4)$*jluids in Sandawa Collapse to the second type or the neutral-pH NaCl brine in Marbel Corridor. The fluids in Wells KN-3 and TM-2D typify the transition between the twofluids, in which* SO_{4res} *is between 80-150 mgkg and* pH_{lab} *is above 4.50.*

The second type offluids have SO„ less than 100 mgkg; its dominant dissolved sulfur species **is** H_2S. H_2CO_3 *is the chemical species controlling the acidity* **of** *the fluids. Upon boiling,* H_2CO_3 *is consumed by the escape* **of** $CO_{2(g)}$ *thus making thefluid pH at near-alkaline level. Both the reservoirfluids are equilibrated with illite, pyrite and chalcopyrite and saturated with calcite. The third type of fluids occurs around the Mt* **Apo** *peak. It contains high dissolved* SO_4, *HSO, and* HCO_3, *low Cl and high gas contents. Thefluids are akin to the shallow-formed acids* of **Bac-Man** *on the basis of low Cl contents and excess Na+K in the solution. It is thereforepostulated that the acid condensates on the shallow level* **of** *Mt. Apo peak* **is** *presently descending to the intermediate depths. The dischargefluidsfrom Well TO-ID typify the third type offluids.*

1.0 INTRODUCTION

Mt. Apo typifies an andesitic volcano that already has gone through its active phase. It belongs to the family of Quaternary volcanoes transecting the central regions of Mindanao island among which include the inactive Mt. Balingasag and the active Mt. Hibok-hibok in Camiguin island. Mt. Apo is presently in a solfataric stage with no new volcanic deposit recorded in the past 5,000 years. Within the period of inactivity, a convecting hydrothermal system developed beneath the Mt. **Apo** volcanic complex. It was first documented by PNOC-EDC in 1983 during their surface exploration in Southern Mindanao. Deep exploratory drilling in 1987 and development drilling in 1992 to 1995 proved that the Mt. Apo hydrothermal system can sustain the ***steam*** requirements for the first 52 MWe power plant and for another **40** MWe power plant. The whole development scheme in Mt. Apo is termed as the Mindanao-1 Geothermal Project (MlGP).

MlGP also encountered acidic fluids during development drilling inside the Sandawa Collapse sector. a topographically depressed geomorphic feature having a diameter of about **5** km. In this paper, we examine the chemical equilibria between fluids and minerals inside the Sandawa Collapse with the objectives of (i) identifying the chemical species contributing to the acidity of the fluids; (ii) relating the secondary minerals to the quality **of** the fluids: and **(iii)** interelating the different **types** of fluids residing inside the Sandawa Collapse.

2.0 THEORETICAL, BASIS

It is a widely accepted theory that modern hydrothermal systems evolved from parental magmatic systems. The transition from magmatic to hydrothermal system involves complex exchanges of chemical species and evolution of different types of secondary minds. The life story of an andesite volcano-hosted hydrothermal system is presented in Figure 1, a cartoon modified after Corbett and Leach (1995). In magmatic systems, where temperatures exceed 500°C, many species exist as neutral complexes rather than ionic compounds. For instance, HCl, NaCl and KCl are present as neutral molecules and the sulfurous gases as H_2S and SO_2 rather than ionised species (Quist and Marshall, 1968). Chemical reactions at magmatic temperatures are, therefore, largely between neutral species. Sulfur is not free to react to form sulfides, and the activity of a metal, such as iron, is controlled by the relative strength of its complexes.

As volcanic activities come to waning stages, reservoir temperature decreases and volatiles are exsolved from the magmatic melt. The exsolved species begin to dissociate in the presence of aqueous medium like HCl and HF. Other species such as SO_2 or CO become unstable and disproportionate into daughter species. Considering other numerous dissociations, the expected pH of the original thermal brine is, therefore, highly acidic. With the increased free H^+, the thermal brine becomes out-of-equilibrium with their host rocks and ultimately leads to rock dissolution or a complex process where the host rocks are dissolved in the acid brine. The acid brines from White Island illustrate the classic case of rock dissolution in magmatic environment. Giggenbach and Glasby (1977) determined that the composition of waters from the White Island volcano crater is very similar in terms of femde element ratios to that of the host andesite, indicating dissolution of the rock during neutralisation of the extremely reactive magmatic fluids. Hedenquist (1987) noted, however, that copper is greatly depleted in the brine from that expected, indicating that copper is being fixed as copper sulfides at depth.

In the original acid brine, sulfur is at oxidation state of +4; Hedenquist (1987) proposed to call this highly oxidising condition as the high *sulfidation* environment. The most dominant dissolved sulfur species is SO_4 and sulfur is deposited as sulfides, sulfates and native sulfur. Alunite and barite also form at high temperature and low pH, and anhydrite under cooler and slightly neutral-pH conditions.

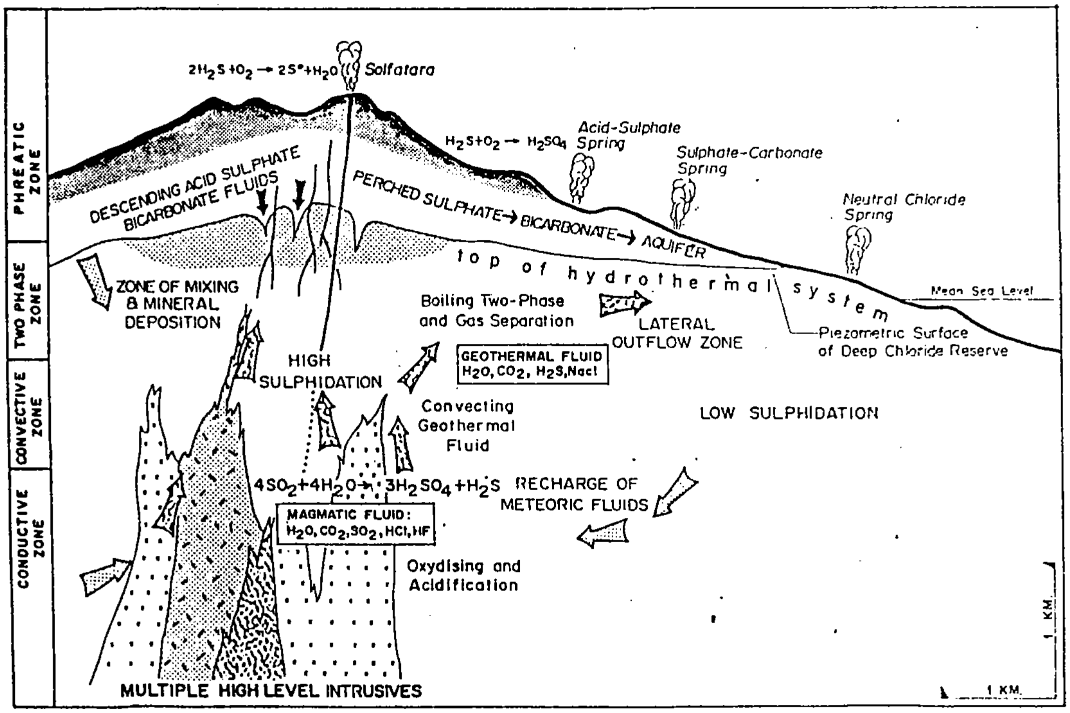

Figure 1: Schematic diagram of andesite volcano-hosted hydrothermal system (Corbett and Leach, 1995)

Through time. the original acid fluids are neutralised because of two factors: (i) decrease of contributions of volatiles from degassing igneous bodies: and (ii) processes of fluid-rock interaction which effectively fix the free H^+ to secondary clays. Evidence of changes in the chemistry of magmatic fluids is observed in the changing composition of the fumaroles in White Island volcano with decrease in temperature from maximum of 1000°C to 500°C. During such period of cooling, the gas chemistry changes from mainly SO_2, HCI, HF and H_2 to one which resembles that of a hydrothermal system. As the fluids flow into permeable channels, they enter the regime of percolating meteoric fluids. The original magmatic constituents are removed by more rock reactions and by dilution of colder fluids. Anhydrite precipitate in joints and thus SO., are removed from the solution. The overall result is the dominance of H_2S as the dissolved sulfur species and NaCl as the dissolved salt. In this case, the sulfur is present at oxidation state of *-2* and therefore termed by Hedenquist **(1987)** as the ***low- sulfdation environment.*** Under these highly reducing conditions, sulfides are the only secondary sulfur containing minerals, with pyrrhotite dominant above 300°C and pyrite at lower temperatures.

On the surface of magmatic and hydrothermal systems. patches to widespread hot to cold altered grounds are common features capping the system. These are products of rock dissolution processes occuring at lower temperature and surface conditions. The acids which dissolve the rocks are formed from the oxydation of exsolved H_2S and they are called as acid-sulfate. steam-heated condensates. There are documented cases, a s in Bac-Man, that these shallow condensates may invade the intermediate depths of a hydrothermal system. The minerals associated with these fluids are low-temperature silica polymorphs and low-temperature clays: collectively. these are termed as the advanced argillic "capping". In areas where the rocks contain **high** grade ore minerals, acid **fluids** may also form with the reaction of cold ground waters with the pre-existing sulfides. This causes the oxide ore zone commonly noted capping the sulfide ore. The resulting mineral assemblages contain alunite, disordered kaolinite, halloysite. allophane and iron oxides. Typically, the alteration occurs as a topographically controlled blankets that often underlie gossans.

3.0 THE EQUILIBRIUM CONDITIONS OF FLUIDS

3.1 Classification of Fluids

The classic Cl-HCO_3-SO_4 ternary plot (Fig. *2)* is used to classify the type of fluids in Sandawa Collapse. Based on the distribution of data in the diagram, we can identify three type of fluids in Sandawa Collapse, namely: (i) the Cl brine represented by the discharge fluids of Wells SK-6D, TM-1D and TM-2D; (ii) the Cl(+SO_4) brine represented by the fluids from Wells KN-ID, KN-2D and KN-3; and (iii) the SO_4-Cl fluids represented by Well TO-ID.

The first type of fluids is what has been known in other geothemal fields as the matured ***neutral-pH*** *NaCl* ***brine*** type which, chemically, has inherent neutral pH and has NaCl as the major salt. In this type of fluids, H_2S is the dominant dissolved *sulfur* species and it can thus be classified as part of the low-sulfidation environment. In Sandawa Collapse, the neutral-pH NaCl brine is found in the western edge and the sector outside of the collapse called the Marbel Comdor.

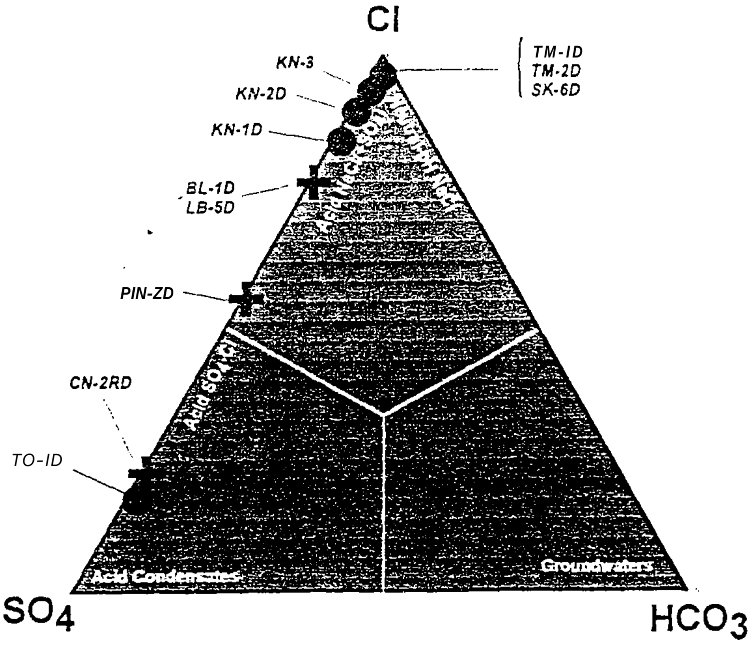

Figure *2:* Cl-HCO_3-SO_4 ternary plot

The second type of fluids is essentially made up of NaCl brine (Take note that the the data points plotted near the Cl apex indicating that the dominant chemical component of the fluids is Cl). However, unlike the first type of fluids, this type contains substantial amounts of SO_{4res} ranging from 132 mg/kg in KN-3 to 653 mg/kg in KN-ID. At surface conditions, the pH level of the fluids is below 5.0. We propose to use the term ***acid NaCl(+SO_4) brine*** to describe this type of fluids.

The third type of fluids is dominated by SO_4 and this is considered part of the high sulfidation environment. At dace conditons, the pH level of the fluids is below 3.0. We propose to call these fluids as the ***acid SO_4-Cl fluids.*** These fluids are akin to the shallow-formed acid SO_4-Cl fluids like that found in Bac-Man geothermal field (see Well CN-2RD in Figure 2).

32 Acidity of the Fluids

In order to identify the most likely source of acidity in Sandawa Collapse fluids, we examine the concentration of selected chemical species presented in Table 2. The HF and free F in the solution are present at very low concentrations of 10^{-5} to 10^{-6} moles/kg that they seem to have minimum, if any, contributions to the acidity of the fluids. In columns 4 and 5, Cl is compared with Na+K. Except in Well TO-1D, there seems to be molal balance between Cl and Na + K indicating that Cl exists as dissolved *salts* (NaCl and KCl) rather than as HCl acid. In the case of Well TO-ID, Na+K exceeds Cl, the same case for the fluids in Well CN-2RD of Bac-Man. The excess Na + K exist as $NaSO_4^-$ and KSO_4^- which compensate the high SO_4 in the solution.

In the last column, it is evident that there is a difference of about an order of magnitude in SO_4 contents between the neutral-pH NaCl brines and the acid fluids. The former type has SO_4 in the order of 10^{-4} to 10^{-5} moles/kg while the later type has SO_4 exceeding 10^{-4} moles/kg. The concentration of SO_4, a product of H_2SO_4 dissociation, apparently controls the acidity of the fluids.

At reservoir conditions, the pH level of the fluids ranges from 5.10 to 5.97 – there is just a narrow range in reservoir pH among different types of fluids even they had contrasting pH at laboratory conditions. For example, KN-ID fluids has laboratory pH of 2.97 but has reservoir pH of ***5.55,*** and SK-6D has laboratory pH of 6.33 but has reservoir pH of 5.97.

The nearness of the reservoir fluid pH is related to the equilibrium constants of the two ***step*** dissociations of H_2SO_4. At lower temperature, H_2SO_4 completely dissociates to SO_4 and $2H^+$ because of high equilibrium constants of its two step dissociations. This will consequently release two moles of free protons for every mole of H_2SO_4 thus making the solution highly acidic. However, at higher temperature, the equilibrium constant of reaction 6 decrease by one order of manitude and reaction 7 by five orders of magnitude. This will practically weaken the *first* and halt the second dissociation ***step*** of H_2SO_4. With only one mole H^+ liberated for every mole H_2SO_4, the fluids at higher temperature will have an apparent neutral-pH *fluids* despite the presence of sulfuric acid

Well	pH_{lab}	pH_{res}	HF	HCO_3	Cl	Na+K	H_2S	HSO_4	SO_4
KN-1D	2.97	5.55	$2.7x10^{-5}$	$8.26x10^{-5}$	0.08	0.08	$3.16x10^{-3}$	$1.29x10^{-3}$	$2.4x10^{-3}$
KN-2D	4.25	5.90	$9.2x10^{-6}$	$1.48x10^{-4}$	0.13	0.13	$1.86x10^{-3}$	$3.45x10^{-4}$	$1.7x10^{-3}$
KN-3	4.85	5.48	$1.7X10^{-5}$	$7.53x10^{-4}$	0.12	0.12	$1.94x10^{-3}$	$2.18x10^{-4}$	$4.2X10^{-4}$
TM-1D	6.55	5.87	n.a.	$3.74x10^{-4}$	0.14	0.14	$3.05x10^{-3}$	$2.64x10^{-5}$	$2.2x10^{-4}$
TM-2D	5.48	5.49	$2.0x10^{-5}$	$2.20x10^{-2}$	0.11	0.11	$2.72x10^{-3}$	$1.10x10^{-4}$	$2.8x10^{-4}$
SK-6D	6.33	5.97	n.a.	$3.72x10^{-4}$	0.10	0.10	$2.57x10^{-3}$	$1.30x10^{-5}$	$1.3x10^{-5}$
TO-1D	3.61	5.10	n.a.	$2.10x10^{-3}$	$4.4x10^{-3}$	$1.1x10^{-2}$	$1.20x10^{-2}$	$2.49x10^{-3}$	$2.4x10^{-3}$

n.a. – not available

Table 1: Concentration at reservoir conditions of selected chemical species in moleskg

In Table 1, the other sulfur species present in significant concentration is the neutral H_2S. On the basis of the concentration of HSO_4, SO_4 and H_2S in the fluids. Sandawa Collapse can be zoned into: (1) ***high sulfidation environment*** where $[HSO_4] + [SO_4]$ exceeds 10^{-3}moles/kg --these are the areas blocked by Wells KN-ID, KN-2D and TO-ID; and (2) ***low sulfidation environment*** where $[HSO_4] + [SO_4]$ is lower than 10^{-3} moleskg, thus, H_2S becomes significantly dominant -- these are the areas blocked by Wells SK-6D, TM-1D, TM-2D and possibly KN-3.

Well KN-3 fluids have the characteristics of both the low and high sulfidation fluids. Their $[HSO_4] + [SO,]$ contents are lower than 10^{-3} but they still have acidic pH level. Owing to these dual characteristics, it is proposed that Well KN-3 represent the transition between an acid NaCl(+SO_4) to neutral-pH NaCl brine. In Figure 4, the above zoning inside the Sandawa Collapse is shown with the iso-SO_{4res} contours. The SO_{4res} concentration of the fluids decrease from east to west possibly explaining why the acidity of well discharges also decreases from east to west.

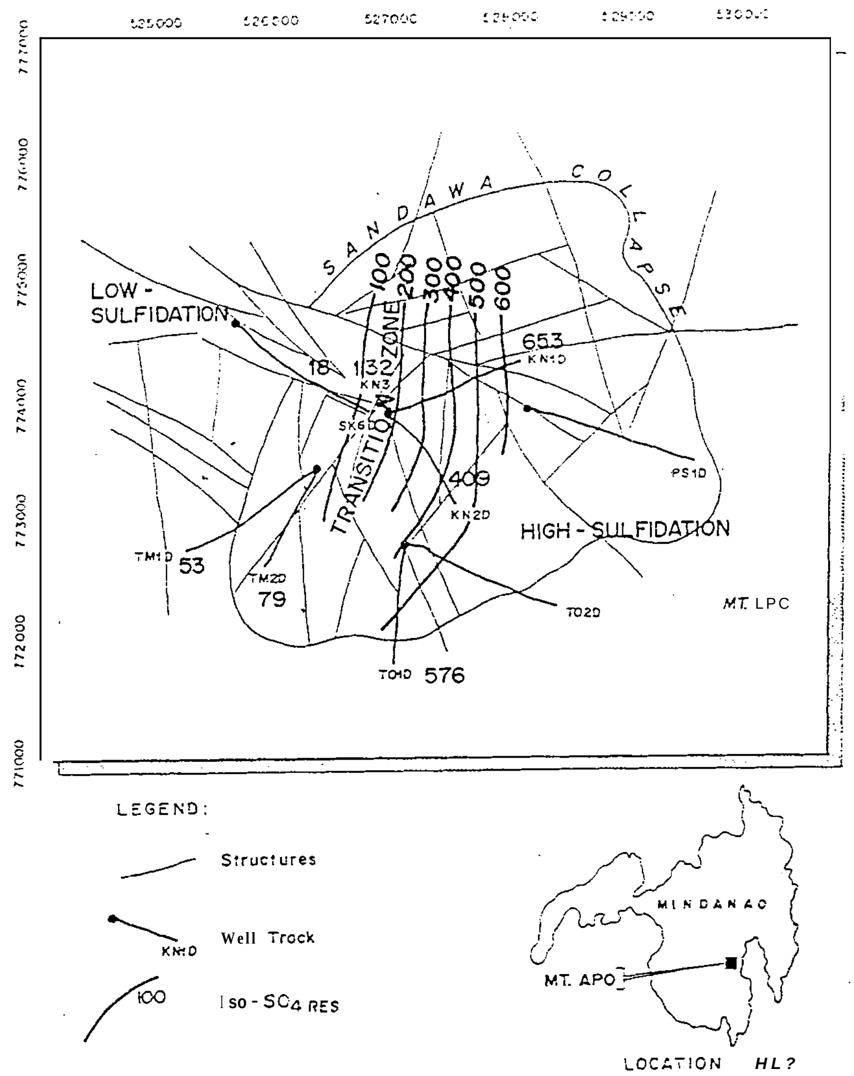

Figure 3: Map showing SO_{4res} contours and zoning inside Sandawa Collapse

3.3 Cation Geoindicators

Rock dissolution processes theoretically free the cations from the rocks. The degree of rock dissolution can be evaluated by examining the equilibrium conditions of the cations in the fluids. In doing so, the cationic ratios of K/Na and K^2/Mg, both of which have corresponding geothermometers (Giggenbach and Gougel, 1989) are compared in the Log(K/Na) vs. Log (K^2/Mg) diagram (Fig. 4). This technique assumes that the congruence of the two geothermometers is the determinant of the full equilibrium conditions of the fluids. In the graph, the equilibrated fluids are represented by the ***fully equilibrated line***. There is also a shaded region in the plot representing the composition of dissolved rock, and a ***partially equilibrated line*** denoting fluids that still are undergoing equilibration processes.

In Figure 4. the neutral-pH NaCl brine (SK-6D, TM-ID and TM-2D) plotted along the fully equilibrated line. The acid fluids from KN-2D and KN-3 also plotted along this line. Since the rate of cation addition is equal to the rate of cation precipitation in equilibrated fluids, it can be generalised that neutralisation processes have practically ceased in neutral-pH NaCl brine, and could be going on in very slow pace in acid NaCl(+SO_4) with relatively low SO_{4res}.contents.

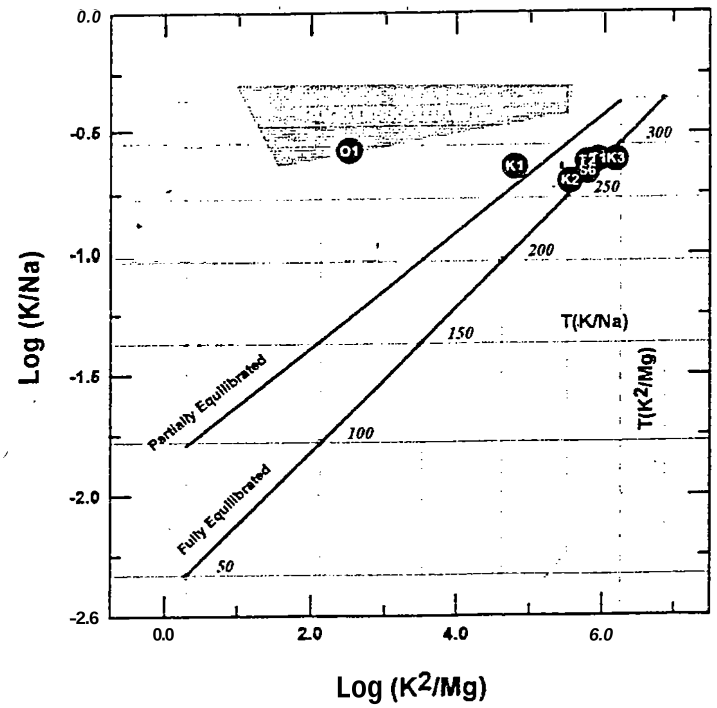

Figure 4: Log(K/Na) vs. Log (K^2/Mg)

The KN-1D fluids plotted near the partially equilibrated line suggesting that the fluids are still approaching full equilibrium conditions. To attain equilibrium, the fluids are removing the excess K, Na and Mg by forming K- Na- and Mg-bearing secondary minerals in the reservoir. These minerals can be illite, albite or chlorite.

Well TO-ID fluids plotted on the rock dissolution region indicating that leaching of Na, K, and Mg from the rocks is actively going on in the area blocked by the well. We therefore expect to find extremely leached rocks, residual silica deposits and Na-, K- and Mg-free clays, called here as the "cation-free clays", in the southern side of Sandawa Collapse. The expected mineral assemblage in this sector include diaspore, pyrophyllite, quartz and possibly alunite.

3.4 Gas Contents of the Fluids

With respect to gas contents, we classify the fluids in the area into low-gas and high-gas fluids. The low gas-fluids are intersected by Wells KN-ID, **KN-2D**, KN-3, TM-1D, TM-2D and SK-3D in the central and western edge of Sandawa Collapse. The high-gas fluids occur in the southern edge of the collapse blocked by Well TO-ID.

The gas zoning in Sandawa Collapse has two important implications. First, epidote as a secondary mineral will be extensively found inside and west of the Sandawa Collapse and not in the southern sector because epidote forms in low-gas zones and rarely in high-gas zones. Second, there must be a reservoir of high-exsolved H_2S and CO_2 on top of the high gas zone which readily will condense or sublimate at near-surface conditions. Condensation will result to the formation of shallow acid SO_4 fluids (and its sublimation to native sulfur. The shallow-formed acids may invade back the reservoir if the hydrostatic pressure of **the deep two-phase** fluids **cannot support** the pressure of descending denser liquid acid condensates. This situation has possibly occured in the area around Mt. Apo peak explaining why the fluids from TO-ID have the chemical characteristics of shallow-formed acids.

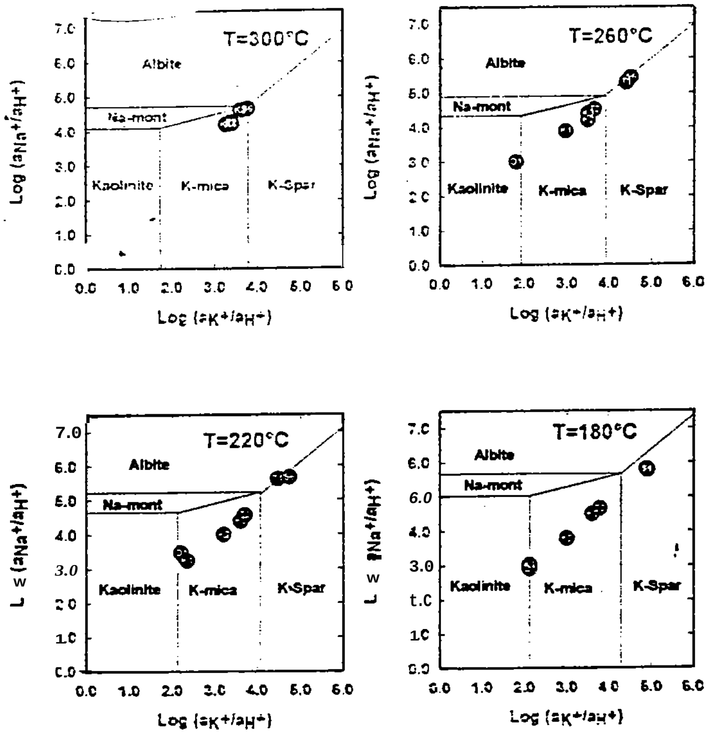

Figure 5: Activity diagrams at different temperatures

4.0 MINERAL EQUILIBRIA

4.1 Silicates

The technique used in evaluating the equilibrium of silicate minerals is the construction of mineral stability diagrams. The use and construction of such diagrams are discussed in detail by Robertson (1984). After setting the stability diagrams at different tempetures (T=300°, T=260°, T=220° and T=180°C), the speciated Na^+, K^+ and H^+ species in the liquids are plotted (Fig. *5).* The trends exhibited by the three types of fluids in Sandawa Collapse are discussed in the succeeding sections.

4.1.1 Neutral-pH NaCl Brine

The data **points** of Well SK-6D and TM-2D at T=300°C and TM-ID at T=260°C plotted on K-mica and K-feldspars stability field. **This** means that if K will be fixed in mineral phase, biotite, illite or adularia will preferentially form. Based on the geologic log **of** the rock cuttings in the wells, biotite and illite are present in the rock cuttings. Upon boiling to temperature of 220°C and 180°C, the mineral equilibria of Wells SK-6D and TM-ID shift to Na-feldspars (albite) and K-feldspar (adularia). Boiling of fluids in the western sector of Sandawa Collapse, therefore will be marked by the presence of secondary adularia and albite in the rock joints.

4.1.2 Acid Na Cl (+SO_4) Brine.

The data **points** of Wells KN-1D, KN-2D and KN-3 at T=300°C, plotted close to the **data** points of the neutral-pH NaCl brine data. Their plots are slightly shifted to K-mica denoting that as the fluids approach full equilibrium conditions, K is fixed to biotite at temperature of 300°C, or illite at 250°C. This is the same conclusion **derived** from the studies of cation geoindicators (Fig. 4).

The plot of boiled fluids of Wells KN-2D and KN-3 at T=260°C and T=180°C remained **fixed** at the K-mica stability field. On the other hand, the data point of Well KN-1D shifted toward kaolinite. This means that boiling the KN-1D fluids extensively will no longer fix Na and K in clays but **will** retain them dissolved in the thermal solution. So instead of illite. we expect to find cation-free clays at temperatures below 180°C.

4.1.3 Acid SO_4-Cl fluids.

The reservoir fluids of TO-ID at T=260°C are in-equilibrium with kaolinite. Most likely, the "cation-free" clays like kaolinite and pyrophyllite are forming in the southern side of Sandawa Collapse instead of K-mica **and** other cation-bearing clays. Even **with** boiling at T=220°C and T=180°C, the fluids are still in-equilibrium with kaolinite, with slight **shift** to K-mica, suggesting that kaolinite and pyrophyllite will **be** found at any temperature regime at the sector blocked **by** Well TO-1D. With the abundant SO_4 in the fluids. any slight shift to K-mica will preferentially form alunite. The well logging results showed that the rocks cuttings from TO-ID indeed contain diaspore, pyrophyllite and alunite (Medrano. **pers.** comm, 1995).

4.2 Quartz, Calcite and Anhydrite Saturation

Calculations of *quartz* saturation with boiling shows that all types of fluids are saturated **with** quartz at reservoir conditions and they all become supersaturated upon boiling. This trend in quartz saturation **has** *two* important implications: (i) quartz geothermometer will be applicable to all types of fluids; and (ii) quartz crystals will be present **as** product of boiling of any type of fluids.

Calculation of the saturation conditions of calcite shows that the neutral-pH NaCl brine **from** Wells SK-6D and TM-ID are saturated with calcite. On the other hand, the acid fluids are undersaturated with calcite. With these characteristics, it *can* be generalised that calcite prefer to stay dissolved at **low** pH conditions.

On the other **hand,** calculation of anhydrite saturation in the fluids shows that the acid fluids of KN-ID, KN-2D and **JSN-3** are anhydrite-saturated, the fluids of Wells TM-1D and TM-2D is slightly saturated and SK-6D **is** unsaturated with anhydrite. The saturation trend of anhydrite seem to follow the trend of the **amounts** SO_4

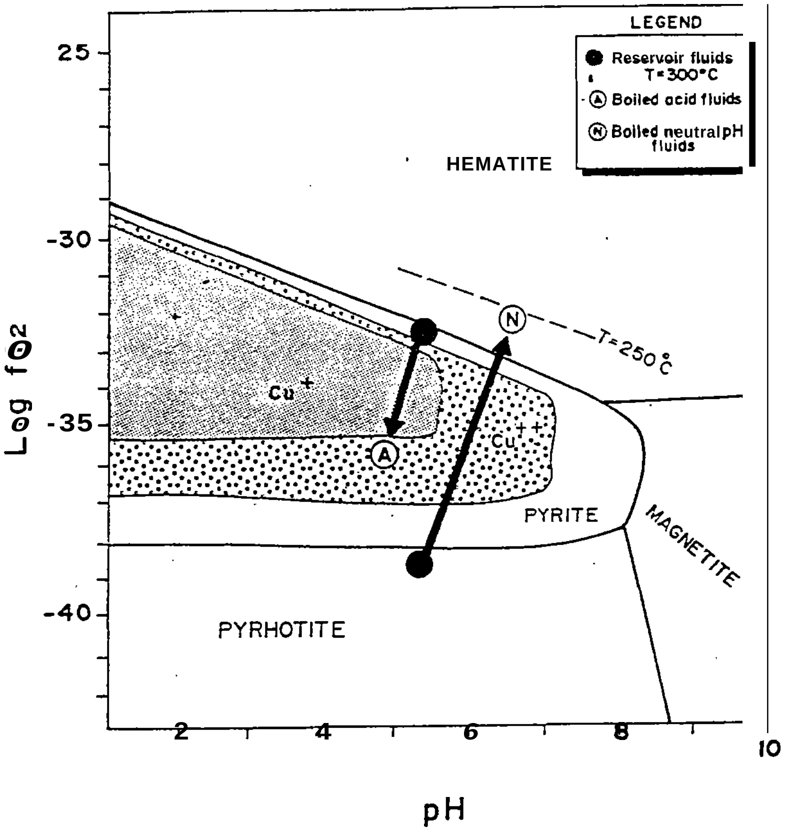

Figure 6: Log fO$_2$ vs. Reservoir pH

(Fig. 3) in the solution. It is apparent that as SO$_{4res}$ increases, the fluids become more saturated with anhydrite. A contra-positive statement is: with precipitation of anhydrite, the SO$_{4res}$ are scrubbed off from the solution and will raise the pH level of the fluids.

4.3 Metallic Sulfides.

The metals present in hydrothermal fluids which participate in forming metallic sulfides are Fe and Cu. The solubilities of Fe and Cu are influenced by the redox state and the pH level of the fluids. In Figure 6, the oxygen fugacity of the fluids is plotted against their pH level. The stability field of some Fe-bearing minerals and the region of Cu-sulfides are also shown in the plot. The outer fringes of Cu-sulfide region are dominated by Cu^{++}- sulfides like chalcopyrite (CuFeS$_2$) and the inner region by Cu^{+} sulfides like bornite (Cu$_5$FeS$_4$). The exact boundary of their stability field is not shown in the diagram but it is apparent that Cu^{+}-sulfides preferentially form in acidic medium.

The neutral-pH NaCl brine plotted on pyrhhotite stable field. Upon boiling to 250C, the equilibrium shift to pyrite. This trend is possibly influenced by the expulsion of H$_2$S$_{(g)}$ from the solution upon boiling leaving SO$_4$ as the dominant dissolved sulfur species. The original reducing fluids become oxidising thus shifting the stable sulfides from pyrhhotite to pyrite. The path of fluids may not be a simple straight line as shown in the diagram. There is also a possibility that the fluids may at one point become in-equilibrium with Cu^{+}-sulfides and Cu^{++}-sulfides. Thus it is possible to find chalcopyrite and rare bornite coexisting with pyrite in neutral-pH conditions.

The acid NaCl(+SO$_4$) fluids are in–equilibrium with pyrite at temperature of 300°C. Because the acid fluids are highly oxidising, the data point almost crosses the hematite stability field. If the fluids are boiled to 250°C, the fluids become more acidic and reducing. The equilibrium path passes through the regions of Cu^{++} and Cu^{+} sulfides. Therefore, in the rocks hosting high-sulfidation environment, we expect to find pyrite + chalcopyrite + bornite as secondary sulfides.

5.0 GENERAL DISCUSSION

5.1 The Acid NaCl(+SO$_4$) Subzone

Figure 7 presents the bounds of subzones of the reservoir and the infered fluid flow path The wells on the center of the Sandawa Collapse namely KN-ID KN-2D and KN-3 encountered the acid NaCl(+SO$_4$) reservoir in Mt Apo geothermal system. This subzone may extend to the north and east following the configuration of the collapse feature. Towards the west, it enters the regime of the neutral-pH fluids and towards the south, it is met by the descending shallow-formed acids.

Chemically, the acid NaCl(+SO_4) **fluids** are composed primarily of dissolved NaCl salt. However. substantial SO_4 is present which apparently control its acidity. In Sandawa Collapse. the SO_{4res} ranges from **652 mg/kg** in the east (KN-1D) to 132 mg/kg in the west (KN-3). Parallel with the SO_{4res} trend, fluid pH at weirbox changes from **highly** acidic (pH= 2.97) in the *east* to slightly acidic (pH = 4.85) in the west establishing **an** imporant correlation that with higher SO_{4res}, the more acidic the fluids will become at surface conditions.

At reservoir temperature of 300°C, the pH level of the fluids **has** a narrow range of 5.48-5.90. The **fluids** initially contain **high** SO_4, HSO_4 and H_2S but low HCO_3 and HS. In this condition, the dissociation rate of H_2SO_4 is determined by the HSO_4 equilibrium. Its reaction donates only a mole of H per mole H_2SO_4 effectively maintaining the reservoir pH at near-neutral level. Upon **boiling** down to 100C, H_2S, HSO_4, HS and HCO_3 in the **fluids** decrease but SO_4 markedly increases. In boiled conditions, H_2SO_4 completely dissociates liberating *2* moles of H^+ per mole of H_2SO_4. Therefore. the apparent neutral-pH reservoir fluids become acidic upon boiling at lower temperature.

With respect to K, **Na,** Mg and pH, the reservoir **fluids** are found to be equilibrated with K-mica which **means** that biotite is inherently forming at reservoir conditions. With extensive boiling, the fluids **with** lower SO_4 remain equilibrated with K-mica but those with **high** SO_4 shift its equilibrium to kaolinite. The cation geoindicators further established that the **high-SO_{4res} fluids** are still in the process of atttaining equilibration. To achieve full-equilibrium, the **fluids** are removing excess Mg by precipitating chlorite. On the other **hand,** the moderate-SO_4 fluids have already attained full-equilibrium conditions that neutralisation process **through** water-rock interaction **has** practically ceased or **still** is going on but at very slow pace. The fluids need to ***go*** through boiling to fully remove the dissolved *sulfur* species **from** the solution and **thus** complete its neutralisation. One product of boiling the fluids **is** precipitation of anhydrite. Another products ***of*** boiling are the Fe-Cu-sulfide minerals whose **formations** reduce the dissolved sulfur in the brine. **In** *summary,* the ideal mineral assemblage formed from boiling the acid NaCl(+SO_4) fluids is:, anhydrite + quartz + pyrite + chalcopyite + bornite.

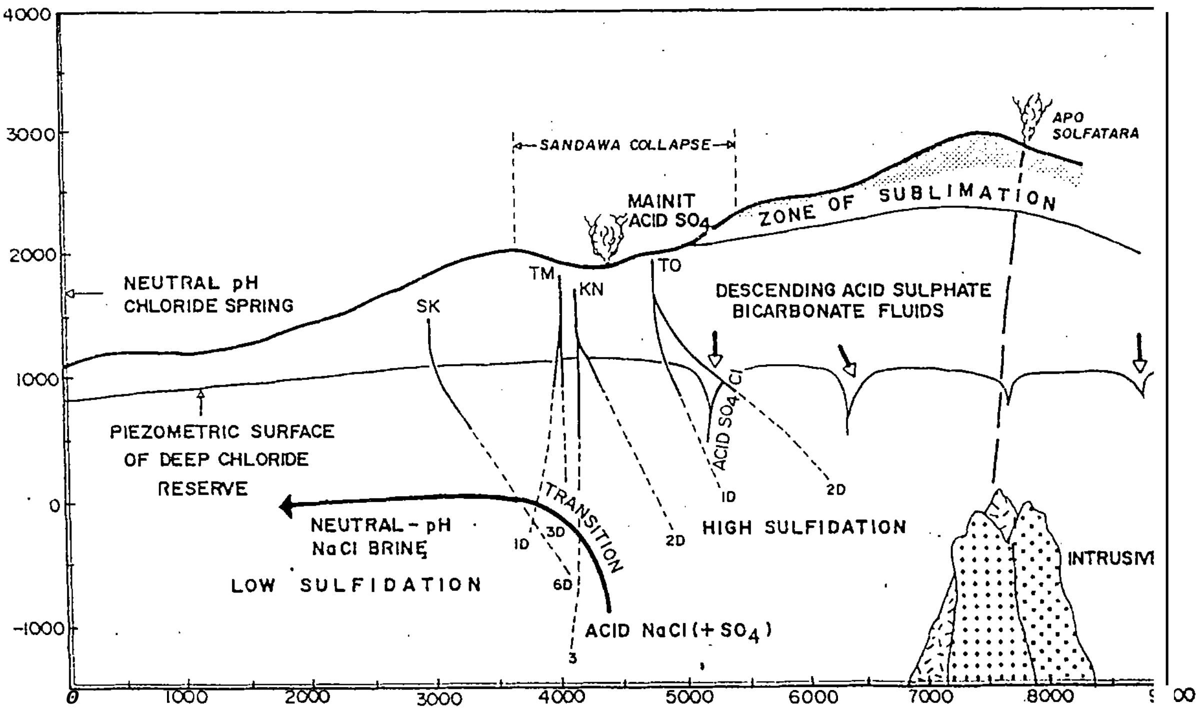

Figure *7:* Conceptual model ***of*** Mt. Apo hydrothermal system

5.2 The Neutral-pH NaCl Subzone

The neutral-pH NaCl fluids occur in the western margins of the Sandawa Collapse up to the northwestern part of the Mt. Apo hydrothermal system. Except for their low SO_{4res}, they are chemically similar with the acid NaCl(+SO_4) fluids. In the boundary of the two subzones, an apparent transition zone exists where the fluids display both the characteristics of acid and neutral-pH brines. In Well KN-3, the SO_{4res} is less than 10^{-3} moles/kg but the pH level becomes slightly acidic upon boiling. In this transition zone, we observe simultaneous precipitation of anhydrite + calcite in the fractures of TM-2D and the stability of HCO_3 concentration fluids even with extensive boiling.

With the above observed chemical field trends, we forward a postulate that the neutral-pH NaCl brine evolved from the acid NaCl(+SO_4) fluids. Removal of dissolved *sulfur* primarily through precipitation of anhydrite and metallic sulfides may have transformed the original acidic fluids in the Sandawa Collapse into neutral-pH fluids in Marbel Corridor. The evolved neutral pH reservoir fluids contain high dissolved H_2S and HCO_3 but low SO_4, HSO_4 and HS. With extensive boiling, H_2S and CO_2 *gases* are expelled fiom the solution, HCO_3 remains stable, and pH rises to near-alkaline level. In this *case*, H_2CO_3 is the main chemical species that controls the acidity of the fluids, hence, liion of dissolved gases from the solution (reactions 9 and 10) shift the fluid pH to higher level.

With respect to their cationic components, the fluids were found to have attained full equilibrium conditions that chemical reactions between the fluids and the rocks are taking place at a very slow rate. Boiling the reservoir fluids upsets the equilibrium which *may* consequently produce quartz + calcite (+adularia) in the rock fractures with pyrite + chalcopyrite and rare bornite. The fluids remain in-equilibrium with K-mica even with estensive boiling indicating that illite will always be present as a secondary mineral in the neutral-pH NaCl subzone from 280°C down to 220°C.

5.3 The Shallow-Formed Acids

Corbett and Leach (1995) explained that high-gas fluids exist at the cores of andesite volcanoes. The exsolved gases above the water table may react with meteoric water to form acids, or may react with oxygen to form native sulfur at solfataras. In Mt. Apo, the fluids proximate to the crater region contain high amounts of gases as proven by the discharge of Well TO-ID and the high well head pressure of Well TO-2D. In addition, solfataras manifest atop the volcano possibly as the product of sublimation of exsolved H_2S from the deep high-*gas* fluids.

The thermal fluids fiom Well TO-1D contain low Cl (158 mg/kg) and high SO_4. In this respect, these fluids are separated from the acid NaCl(+SO_4) fluids in Sandawa Collapse which have high Cl (4000 mg/kg) contents. The fluids were also found to have more dissolved Na+K over Cl which discounted the possible occurrence of HCl or *any* newly-supplied magmatic volatiles. With all its chemical characteristics, the fluids in TO-1D are thought to be product of *steam* condensation atop the high-gas fluids in the core of Mt. Apo. These SO_4-rich shallow-formed acids are evidently descending to the intermediate depths of the geothermal system.

6.0 CONCLUSIONS

Three types of fluids reside inside the Sandawa Collapse, namely, the acid NaCl(+SO_4), the neutral-pH NaCl brine and the acid SO_4-Cl fluids. The first type of fluids occupies the central sector of Sandawa Collapse. It contains high amounts of dissolved SO_4 and HSO_4 which appears to be controlling the acidity *of* the fluids. Neutralisation processes through deposition of sulfur-bearing minerals like pyrite, chalcopyrite, bornite and anhydrite effectively cleanse the fluids of dissolved sulfur species thus shifting the fluid pH to neutral level. From originally acid fluids, neutralisation processes transform the acid, NaCl(+SO_4) to the second type or the neutral-pH NaCl brine.

The second type of fluids have SO_{4res} less than 100 mgkg; its dominant dissolved *sulfur* species is H_2S. H_2CO_3 *is* the chemical species controlling the acidity of the fluids, which upon boiling is consumed by escape of

$CO_{2(g)}$ thus making the fluid pH at near-alkaline level. The fluids are equilibrated with illite. pyrite and chalcopyrite.

The third type of fluids occurs around the Mt Apo peak. It contains **high** dissolved SO_4. HSO_4 and HCO_3. low Cl and **high** gas contents. The fluids are akin to the shallow-formed acids of Bac-Man on the basis of low Cl contents and excess Na+K in the solution. It is therefore postulated that the acid condensates on the shallow level of Mt. Apo peak is presently descending to the intermediate depths. The discharge **fluids** from Well TO-1D typify the third type of fluids.

REFERENCES

Amorsson, S., 1995. A summary of basic thermodynamic relations and the methodology of calculating the thermodynamic properties of minerals at different temperatures and pressures. Science Institute, University of Iceland.

Arnorsson, S.. Sigurdsson, S. and Svavarrsson, H., 1982. The geochemistry of geothermal waters in Iceland I. Calculations of aqueos speciation from 0° to 370". Geochimica et Cosmochimica Acta Vol. 46, pp. 1313 to **1532.**

Corbett, G.J. and Leach **T.M.,** 1995. SW Pacific Rim Au/Cu System: Structure, Alteration and Mineralisation. **A** workshop presented in the Philippines.

Giggenbach, **W.F.,** 1982. The chemical and isotopic composition of gas discharges fiom New Zealand andesitic volcanoes: Bulletin Volcanologiques, 45, 253-255.

Giggenbach W.F. and Glasby. G.P., 1977. The influence of thermal activity on the trace metal distribution in **marine** sediments around White Island, New Zealand: NZ DSIR Bulletin 218, 121-126.

Hedenquist, J.W., 1987. Epithermal Gold. PNOC-EDC Internal Compilation.

Jao, G.T. and Batnag R.E., 1995. Characterisation of the Chemistry of Acid Fluids in PNOC Geothermal Fields. PNOC-EDC Internal Report.

PNOC-EDC Geoscientific Staff, 1994. Mindano-1 Geothermal Project. Resource Assessment Update. PNOC-EDC Internal Report.

Quist, AS and Marshall, WC, 1968. Electrical conductances of aquous sodium chloride from 0" to 800°C and at pressures to 400 bars. Journal of Physical Chemistry, v. 72. p.684-703.

Robertson, J.M. *(ed.)*,1984. Fluid Mineral Equilibria in Hydrothermal Systems. Reviews in Economic Geology Vol. 1.

Salonga N.D. and Sempio C.R. 1994. Geochemistry of vapour discharges of MIGP well discharges. PNOC-EDC Internal Report.

Authors note: Thefollowing sysmbols were used ***in*** *the diagrams: K1 -- KN1D; K2 -- KN2D; K3 -- KN3; TI -- ?WID; T2 -- TM2D;* ***O1*** *-- TO1D; S6 -- SK6D*