CHEMICAL CHARACTERISTICS OF ACID FLUIDS IN SOME PNOC GEOTHERMAL WELLS

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Abstract

Wells drilled above and within the margins of upflow regions in most PNOC-EDC geothermal fields produced acid fluids during initial discharge tests. The acid wells commonly discharged SO_4*-rich waters with varying amount of Cl and dissolved cations. Waters from very hot (>280°C) reservoir contain excess Cl concentrations, suggesting that their acidity is partly caused by HCl from, most likely, a volcanic source. In most wells, the dissociation of* HSO_4^- *results to a sharp decline in pH as the fluids ascend. Boiling models also show that for reservoir waters with substantial amount of* HCO_3^- *pH increases as a result of boiling. This is due to exsolution of* CO_2 *into the steam phase. In general, except for the magmatic reservoir waters which have inherently low pH at depths, fluid pH at reservoir conditions is about 5.0 which is near-neutral at high temperature conditions (T>250°C).*

1.0 INTRODUCTION

In various fields that are being explored, developed and exploited by PNOC-EDC (Fig. 1), a number of wells produced acid fluids during initial flow tests, hours to few days from the start of fluid discharge. These wells are located above or within the upflow-outflow margins of the geothermal systems. Most of them were drilled adjacent to volcanic features like domes such as in Mt. Labo and Southern Negros; or within structures like craters and collapse such as in Mt. Apo, Leyte (Mahanagdong and Alto Peak) and Bacon-Manito.

The occurrence of corrosive flluids in Philippine geothermal systems has been discussed and evaluated by several geochemists (Solis, 1988; Ruaya et al., 1991; Ramos-Candelaria, 1992; Salonga, 1995; Parilla et al., 1995; PNOC-EDC, 1994-1995). This paper presents a synopsis of a large chemical database of selected wells from production fields (BGPF, SNGF), development fields (Alto Peak and Mahanagdong in Leyte; Mt. Apo in Mindanao) and an exploration area (Mt. Labo, southern Luzon). Wells drilled in Mt. Pinatubo in 1989 before it erupted in 1991 were also included to represent acid waters with active magmatic input (Ruaya et al., 1991). The collation of these chemical data is intended to: 1) characterise the fluid chemistry of acidic reservoir waters, 2) identify the chemical species contributing to the fluid acidity. and 3) evaluate the effects of boiling on pH.

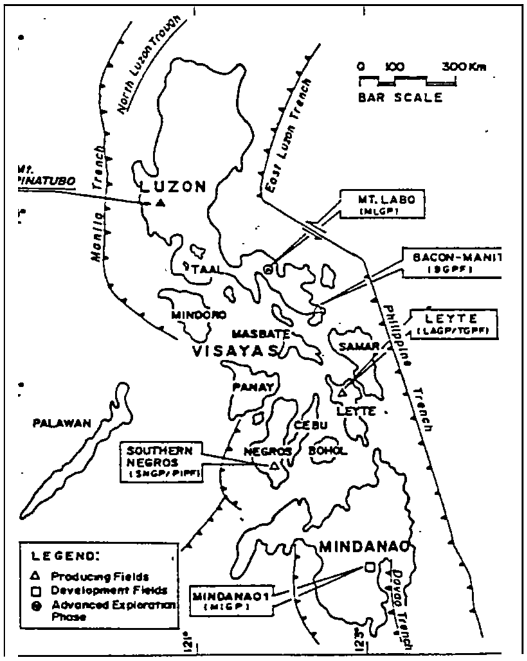

Fig. 1 Location map of PNOC-EDC geothermal project sites cited in this paper

2.0 WATER CHEMISTRY

Most of the wells discharged acid Cl-SO, type of water based on pH and relative concentration of Cl, SO_4 and HCO_3 (Fig. 2). Some of them (i.e. MG-9D, PIN-3D, AP-7D) which originate from very hot (>280°C) reservoir are characterised by excess Cl^- content, suggesting that their acidity is partly introduced by HCl from, most likely, a volcanic source. The representative chemistry of water samples are shown in Table 1. Acid Cl-SO_4 waters with no excess Cl appear to have relatively higher amount of SO_4 (>1000 mg/kg) than those with excess Cl except PIN-2D. The acid SO_4-Cl waters show intermediate SO_4 levels (-800 mg/kg).

Laboratory pH (at 25°C) ranges from about 2.0 (AP-7D) to 5.0 (EL-ID). Although significant variations are shown by Mg and Fe (Table 1), they are considerably high compared to typical neutral pH fluids which normally contain less than 1.0 ppm of both species. Part of the Fe content is probably derived from casing corrosion. Generally, Na, K and SiO_2 are consistently high. Well PIN-3D waters contain exceptionally high concentrations of cations (Na, K, Ca) which are apparently leached from the reservoir rocks. *On* the other hand, Well CN-2RD in Bacon-Manito shows the lowest Na, K and Cl but also high SO_4, which typifies the acid SO_4-Cl waters. These fluids were derived from the oxidation of H_2S at shallow, near-surface depths which migrates downwards into the reservoir, producing the extensive near-surface acid alteration zones in the Cawayan sector of the Bacon-Manito geothermal field (Solis, 1988)

Well AP-7D (Alto Peak) discharged steamdominated fluids with Cl concentration of only 2058 mgkg which is lower than the Cl level in adjacent wells (AP-2D, 3500 mg/kg). Steam condensates apparently form during discharge of these wells, and dilute the upflowing Cl waters which also results to lower Na, K and Cl not reflective of their high-temperature source.

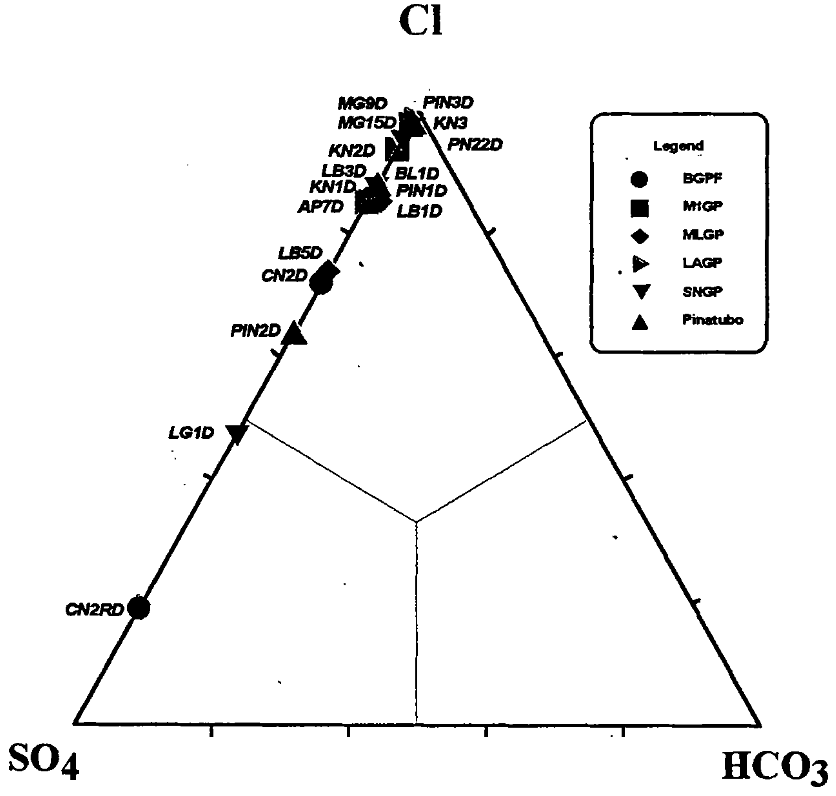

Fig. 2 Cl-SO4-HCO3 Ternary Plot

Table 1 Representative Discharge Water Chemistry

Fluid Type	Well Name	pH (25°C)	Cl	SO.	Na	K	Mg	Fe	Ca	SiO_2	Cl/SO_4	Temperature (°C)			
							(ppm)					TNa-K	$TSi0_2$	TNa-K-Ca	Max Meas
low Cl high SO_4	CN-2RD	4.83	206	871	455	46	8.2	4.25	17	638	1	189	246	199	250
	LG-1D	3.95	769	860	580	190	2.7	145	8	951	2	345	270	293	240
high Cl high SO_4 (Cl>Na+K)	MG-9D	3.11	7940	74	4283	1200	21	77	115	1128	290	325	299	299	305
	MG-15D	3.66	5663	136	3080	747	13	31	60	1000	112	307	286	287	280
	AP-7D	2.08	2058	347	840	130	24	469	33	871	16	258	271	229	320
	PIN-2D	2.26	4474	2491	2850	516	223	780	69	1233	4	274	231	261	330
	PIN-3D	255	37760	500	17400	3540	133	525	2207	1660	205	287	176	271	330
	KN-2D	4.25	9625	597	5780	1103	2	9	64	978	44	279	272	283	300
	KN-3	4.85	10741	192	5573	1554	0.51	0.87	163	1145	151	323	296	300	320
	BL-1D	4.91	2922	410	1660	384	0.15	-	8	1018	19	301	265	291	310
	PN-22D	3.75	5316	258	3020	680	3.28	-	24	1148	55	298	215	294	295
high Cl high SO_4 (Na+K≥Cl)	KN-1D	2.40	6638	1125	3785	865	10	121	10	1136	15	300	294	312	300
	CN-2D	3.79	4272	1635	2910	275	9	189	7	592	7	182	241	242	240
	LB-1D	3.48	7517	1089	4527	643	119	145	37 .	1105	18	249	295	261	279
	LB-3D	3.46	6713	975	3975	520	23	7	7	837	18	218	270	274	264
	LB-5D	3.04	5877	2036	3738	523	183	233	2	863	7	248	273	297	254
	PIN-1	4.10	10104	1309	6070	608	162	86	98	555	20	217	240	234	265

3.0 STEAM CHEMISTRY

The amount of CO_2 in the *steam* discharges (Table 2) varies from about 86% vol (LG-1D) to as high as 98% vol (PIN-3D), while H_2S ranges fiom 1.5% (PIN-3D) to as much as 11.8% (KN-ID). Well AP-7D and PIN-3D yield very high level of H_2S (>300 mmoles/100 moles steam), suggesting relative proximity to or more direct communication with a degassing magmatic body. In general, magmatic fluids (AP-7D/PIN-3D) and those originating from reservoirs with temperatures less than 300°C are associated with higher levels of CO_2 and H_2S.

An assessment of the probable origin of the gases is shown in Figure 3. The gases, apparently. are of diversed origins. For example, the very high amount of CO_2 and the significant concentration of CH_4 in CN-2D were probably partly derived from the sediments underlying the Pocdol Volcanics in the Bacon-Manito geothermal field The magmatic gases **fiom** Mt. Pinatubo (Ruaya et.al., 1991), on the other hand contain very low CH_4, very high CO_2 and substantial N_2. The very low concentration of CH_4 and of the other gases in Mt. Apo wells (KN), however, is more likely due to prolonged interaction of the gases with the rocks and the water within a large structural depression known as the Sandawa Collapse.

The concentration of CO_2 and H_2S are correlated with source temperature in Figure 4. Generally, wells with higher temperatures discharged *steam* with lower CO_2/H_2S ratios and waters with relatively lower pH. This implies that, at lower temperatures, more CO_2 are dissolved than H_2S. Except in a degassed region like the Sandawa collapse in Mt. Apo, H_2S appears to be more concentrated in the hotter part of the geothermal reservoir.

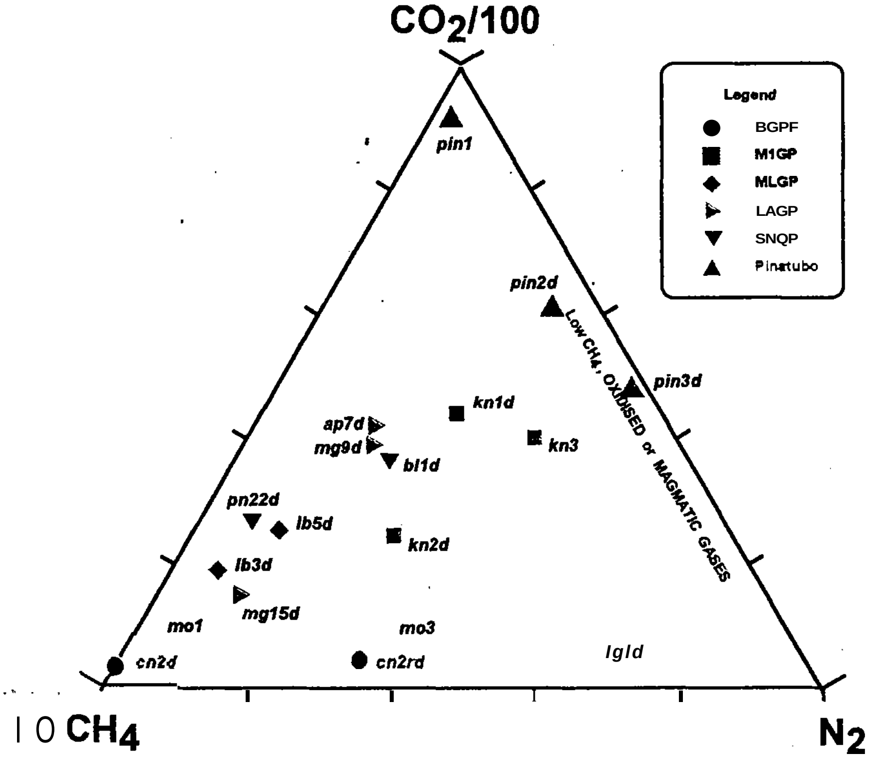

Fig. 3 CO_2 - CH_4 - N_2 Ternary Plot

Table 2 Representative Steam Discharge Chemistry

Water Type	Well Name	pH (25°C)	WHP (MPaa)	H (KJ/KG)	SP (MPaa)	CO_2	H_2S	NH_3	He	H_2	Ar	N_2	CH_4	Cl
low Cl high SO,	CN-2RD	4.83	0.514	965	0.433	419	16	2.01		3.45	0.47	30.4	5.58	
	LG-1D	3.95	0.89	2002	0.87	753	36	1.34	2.00	5.29		77.72	3.52	11
high Cl high SO_4 (Cl>Na+K)	MG-9D	3.11	0.63	1610	0.56	549	32	0.06		0.37		2.61	0.60	14
	MG-15D	3.66	0.95	1364	0.84	833	32	0.20		1.17		6.65	4.05	27
	AP-7D	2.08	3.65	1455	1.46	2347	359	0.03	0.002	17.38		9.63	2.27	105
	PIN-2D	2.26	0.723	1907	0.62	2758	165	0.01		6.12	0.01	14.37	0.289	
	PIN-3D	2.55	0.12	2439	0.113	43597	651	0.22	0.007	64.8	0.51	446	1.a7	
	KN-2D	4.25	0.172	2116	0.158	97	9	0.07	0.012	0.039	0.023	1.12	0.185	15
	KN-3	4.85	1.203	1990	0.428	144	16	0.1	0.04	0.008	0.005	1.44	*0.07*	90
	BL-ID	4.91	3.81	1978	0.548	401	22			1.52	-	2.42	0.46	
	PN-22D	3.75	2.61	2048	2.59	334	18	15.15		1.31		0.963	0.825	
high Cl high SO, (Cl<Na+K)	KN-1D	2.40	0.88	1883	0.738	135	18	0.01		0.734		0.838	0.087	17
	CN-2D	3.79	0.68	1058	0.649	24354	89			19.86		312	737	
	LB-1D	3.48	0.575	1213	0.423	2472	130	0.15						
	LB-3D	3.46	1.061	1207	0.826	3676	145		0.103	1.96	1.56	13.14	14.27	
	LB-5D	3.04	0.347	1193	0.251	1157	36			3.81	0.07	5.51	2.83	
	PIN-I	4.10	0.172	1758	0.162	2789	61	0.01		0.233		0.891	0.161	

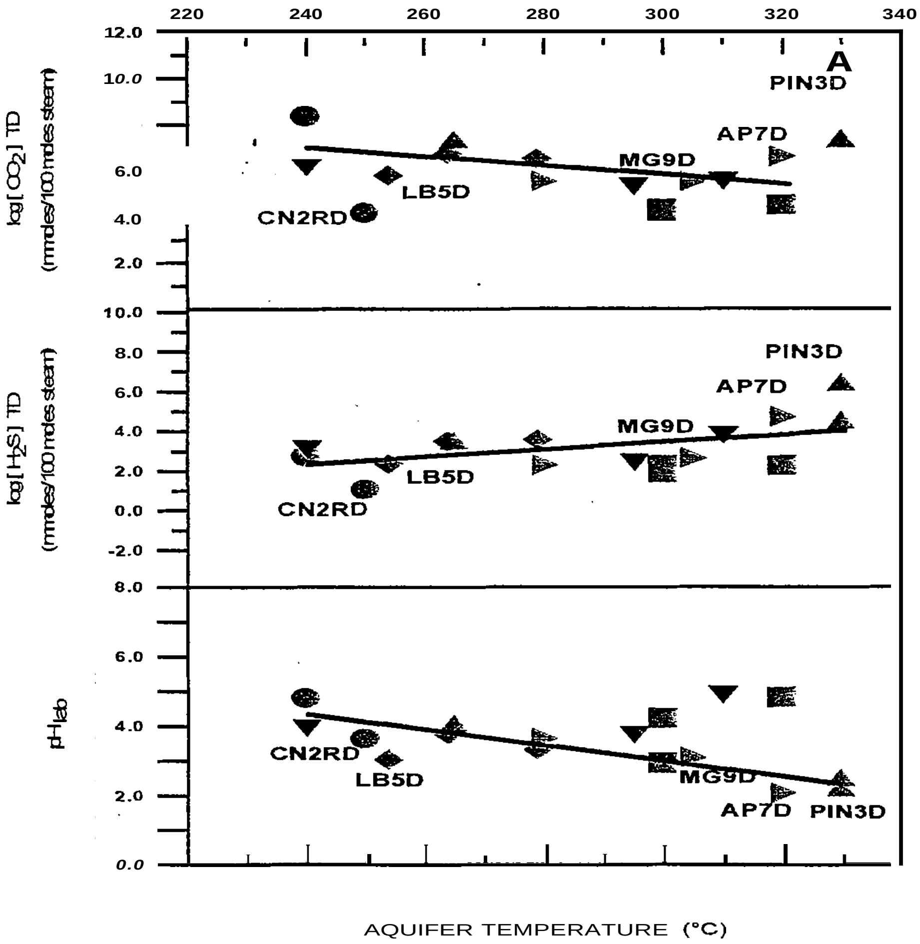

Fig. 4 pH, CO_2, H_2S vs. Temperature

4.0 FLUID ACIDITY

The pH and concentrations of the different chemical species at reservoir conditions were calculated using the speciation software WATCH 2.1 (Amorsson. 1990). Dissolved sulfur species and other constituents that may be contributing to fluid acidity are presented in Table 3. Only wells AP-6D and PIN-3D showed inherently low pH of less than 3.5. For all the other wells. the reservoir pH does not vary much, being close to approximately 5.0. Laboratory pH, however, varies significantly. The changes in pH with temperature were evaluated through boiling models using WATCH 2.1. The changes in pH with temperature are shown in Figure 4. Three general trends were observed.

The first trend shows increase in pH up to about 6.0 until 100°C before it drops to 3.8-4.8 upon conductive cooling down to 25°C. This was exhibited by by wells KN-3, BL-ID and PN-22D. In these wells, the $HCO3^-$ reservoir concentration is almost of the same level with $HSO4^-$ and $SO4^{2-}$. The increase in pH *can* be attributed to the exsolution of CO_2 from the liquid during boiling. The second trend is a continuous and sharp decline of pH with decreasing temperature. This is exhibited by wells where HCO_3^- is relatively lower than SO_4^{2-} and HSO_4^- and SO_4^{2-} is most dominant. The behaviour of pH in wells LG-1D, CN-2D KN-2D and MG-15D appears to be intermediate between the first and the second trends. The third trend is a very gradual decline of inherently low pH in wells AP-7D and PIN-3D. In these wells, HSO_4^- is the most dominant specie. and excess Cl may be substantial enough to affect the fluid pH (Table 3).

Table 3 Reservoir Concentrations of Selected Chemical Species

Water Type	Well Name	pH (25°C)	pH (res)	Meas. Temp. (°C)	HSO4	SO4	HS	H2S	HCO3	HF	F	Cl	Na+K
low Cl high SO_4	CN-2RD	4.83	5.8	250	6.10E-04	4.40E-03	9.70E-06	3.07E-04	1.47E-04		-	4.02E-03	1.34E-02
	LG-1D	3.95	5.2	240	9.90E-04	2.59E-03	9.18E-05	9.04E-03	8.18E-04		-	1.11E-02	1.56E-02
high Cl high SO_4 (Cl>Na+K)	MG-9D	3.11	5.09	305	1.30E-03	7.19E-04	24E-06	4.58E-03	8.07E-05	8.91E-05	1.98E-05	9.35E-02	8.30E-02
	MG-15D	3.66	4.63	280	4.59E-04	l.70E-04	38E-06	4.34E-03	7.78E-05	5.71E-05	7 66E-06	9.06E-02	8.46E-02
	AP-7D	2.08	2.56	320	1.94E-03	1.04E-06	36E-07	8.97E-02	1.02E-06	2.38E-05	8.67E-09	2.70E-02	1.74E-02
	PIN-2D	2.26	5.31	330	7.23E-03	3.20E-03	4.66E-05	340E-M	5.37E-04	7.24E-05	1.50E-05	5.51E-02	5.32E-02
	PIN-3D	2.55	3.22	330	1.69E-03	3.13E-05	8.04E-07	3.57E-M	3.40E-05			4.71E-01	3.21E-01
	KN-2D	4.25	5.90	300	3.45E-04	1.70E-03	[illegible]	1.86E-03	1.48E-04	9.27E-06	1.60E-05	1.29E-01	1.12E-01
	KN-3	4.85	5.48	320	2.18E-04	4.19E-04	[illegible]	1.94E-03	7.53E-04	1.69E-05	1.13E-05	1.25E-01	1.20E-01
	BL-1D	4.91	5.31	310	1.15E-03	6.92E-04	1.14E-05	4.02E-03	l.10E-04			3.35E-02	3.20E-02
	PN-22D	3.75	5.12	295	6.43E-04	4.38E-04	4.88E-07	1 97E-04	5.12E-05		-	7.05E-02	6.88E-02
high Cl high SO_4 (Cl<Na+K)	KN-1D	240	5.56	300	1.29E-03	2 -03	4.18E-05	3.16E-03	8.26E-05	2.73E-05	2.00E-05	8.45E-02	8.82E-02
	CN-2D	3.79	4.81	240	3.36E-03	4 -03	2.25E-05	6 84E-03	3.37E-03			7.70E-02	9.07E-02
	LB-1D	3.48	5.09	279	1.67E-03	2.23E-03	8.24E-05	2 08E-02	8.83E-04	5.30E-05	2.25E-05	1.15E-01	1.13E-01
	LB-3D	3.40	4.97	264	1.42E-03	2.56E-03	7.91E-05	1.60E-02	1.12E-03	2.98E-05	1.52E-05	1.23E-01	1.19E-01
	LB-5D	3.04	5.14	254	2.03E-03	3	[illegible].94E-05	5 43 -03	7.06E-04	3.37E-05	2.51E-05	1.02E-01	1.09E-01
	PIN-1	4.10	4.93	205	1.87E-03	3	[illegible] 33E-05	[illegible]-02	1.43E-03	4.94E-05	2.11E-05	1.41E-01	1.41E-01

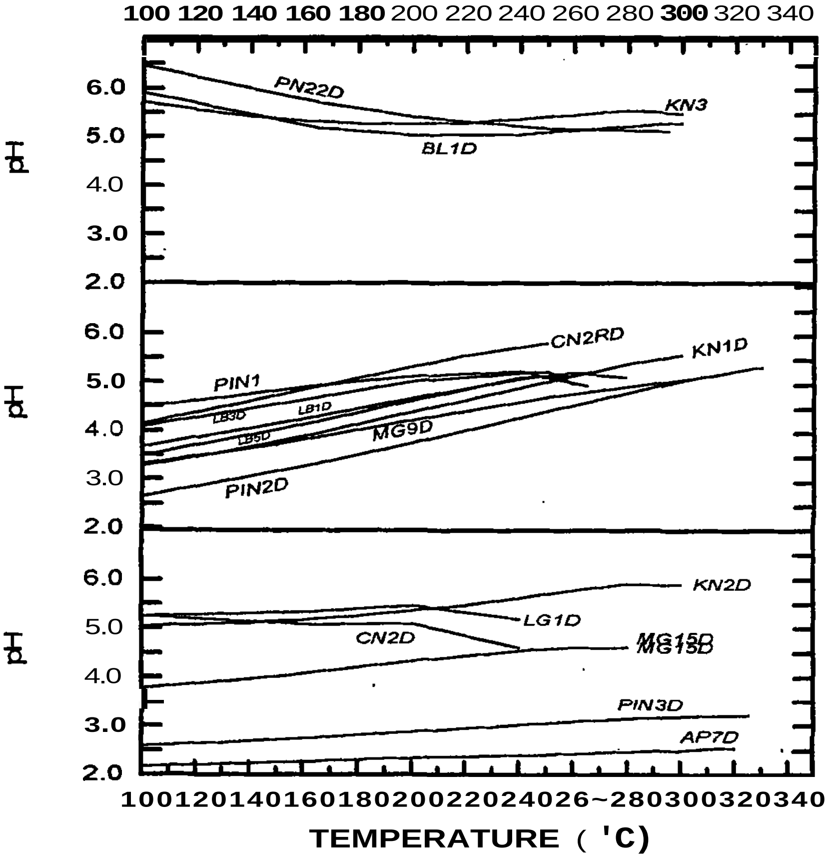

Fig. 5 Change in pH with Temperature

5.0 SUMMARY

Acid Cl-SO_4 **fluids** with excess Cl are associated to reservoirs with temperatures exceeding 280°C. They are characterised by lower amount of SO, (<600 mgkg) compared to those with no excess Cl (SO_4>1000 mgkg) which, on the other **hand** originate from reservoirs **with** temperatures of 240°-280°C. The latter, however, can be associated with higher CO_2 and/or CO_2/H_2S ratios. Acid SO_4-Cl waters in PNOC wells are characterised by low Cl (<1000 mg/kg), low Na and K, and SO_4 of about 800-900 mgkg.

At reservoir conditions, pH is generally near-neutral (5 to 6) except for magmatic **fluids** (pH<3.5). In contrast. laboratory pH shows significant range from 2.26 to 4.91. Boiling models showed contrasting trends of change in pH with temperature. Increase in pH is exhibited **by** wells whch have substantial concentration of HCO_3. The rise in pH is apparently due to the exsolution of CO_2 from the liquid phase dunng boiling. For wells with HSO_4 and SO_4 as the dominant species, pH continuously drops. At temperatures lower than 100°C, pH declines due to increased dissociation of HSO_4 which outweighs the effect of the loss of CO_2 in the water.

ACKNOWLEDGMENT

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LIST OF REFERENCES

Amorsson, S, (1990). WATCH 2.1 - A speciation software.

D'Amore, F. (1991). Application of Geochemistry in Reservoir Development. UNITAR/UNDP Publication. Rome, Italy.

Parilla, E.V., Jordan, O.T. and Ruaya, J.R. (1995). Mahanagdong Geothermal Field, Leyte Geothermal Power Project - Geochemistry Resource Assessment Update. PNOC-EDC Internal Report.

PNOC-EDC (1994a). Bacon-Manit0 Geothermal Production Field Pre-exploitation Baseline Geochemistry Data.

_________ (1994b). Mindanao-1 Geothermal Project- Resource Assessment Update.

_________ (1995). Mt. Labo Geothermal Project - Resource Assssment Update (Draft Report)

Ramos-Candelaria, M.N. (1992). Geochemical Assessment of South Lagunao and Baslay-Dauin, SNGP. PNOC-EDC Internal Report.

Ruaya, J.R., Ramos, M.N. **and** Gonfiantini, R. (1991). Assessment of Magmatic Components of the Fluids at Mt. Pinatubo Volcanic-geothermal system, Philippines From Chemical and Isotopic Data. A Paper presented to a Seminar on "Magmatic Contributions to Hydrothermal Systems, 10-16 November, 1991, Japan.

Solis, R.P. (1988). Chemical Signatures **of** Acidic Fluids in the Production Wells of Bacon-Manit0 Geothermal Project. PNOC-EDC Internal Report.

Salonga, N.D. (1995). Fluid-Mineral Equilibria in Acid NaCl ($+SO_4$) Reservoir: Sandaw Collapse, Mt. Apo Hydrothermal System. PNOC-EDC Internal Report.

Truesdell: A. H. (1991). Origin of Acid Fluids in Geothermal Reservoirs. Geothermal Resources Council Transactions, 15.