

NOTICE CONCERNING COPYRIGHT RESTRICTIONS

This document may contain copyrighted materials. These materials have been made available for use in research, teaching, and private study, but may not be used for any commercial purpose. Users may not otherwise copy, reproduce, retransmit, distribute, publish, commercially exploit or otherwise transfer any material.

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specific conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use," that user may be liable for copyright infringement.

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

A Review of the Origin of Sulphur In DN-1 Discharge and Its Implication for Future Development, Dauin Prospect, Central Philippines

L.F. Bayrante, D. Z. Hermoso, M. R. Candelaria, P. I. Pamatian and A. V. Mejorada
PNOC-Energy Development Corporation,
Fort Bonifacio Makati City, Philippines

ABSTRACT

Well DN-1, the first exploratory well of the Dauin geothermal prospect discharged in 1983 substantial quantities of sulphur with a near-neutral pH fluid (pH 6.4 to 7.2) containing maximum chloride levels of 3,300 mg/kg, SO₄ of 300 mg/kg; and high CO₂ and H₂S relative to the production wells in Palinpinon Field to the north. The chemistry of DN-1 discharge-fluid and the origin of sulphur have been the cause of apprehension for any future development due to concerns on the presence of a possible acid resource southeast of Cuernos de Negros. A reinterpretation of the previous and new surface data was undertaken in 1992 and 1996, including the origin of sulphur, to evaluate the potential of Dauin for development. The results indicate that the sulphur in DN-1 is formed from partial oxidation of hydrogen sulphide derived from the neutralised-acid fluids formed by sulphur hydrolysis at shallow levels but distant from DN-1. The study argues for the presence of near neutral exploitable resource in the prospect area.

Introduction

The Dauin geothermal prospect is located about 5 km. southeast of the Palinpinon geothermal field (Figure 1). The prospect is separated by the 1,800 m-high Cuernos de Negros, a composite andesite volcano of Quaternary to Recent age. Two wells, DN-1 and DN-2, were drilled in the area between 1982 to 1983 to test its potential for geothermal development. Between the two wells, well DN-1 encountered relatively high temperature (240°C) and near neutral fluids with maximum reservoir Cl of 3,300 mg/kg (Bayrante et al., this vol.). This well also discharged substantial amount of elemental sulphur forming localised sulphur fall-outs that covered the immediate vicinity of the well pad and the containment sump used during discharge testing.

The presence of sulphur in DN-1 and pronounced corrosion and erosion of the surface discharge facilities became a major deterrent to any exploration activity in the area drilled by DN-1. As a result DN-2, the second deep exploratory well, was drilled about 4 km southwest of DN-1 instead of its original target location sited about 2 km southwest of the first well. It was argued previously that the data from well DN-1 and the acid nature of most thermal discharges indicate an acid resource southeast of Cuernos de Negros. This paper aims to review the possible origin of sulphur in the DN-1 discharge to determine its possible origin and to evaluate the potential of the area for future development.

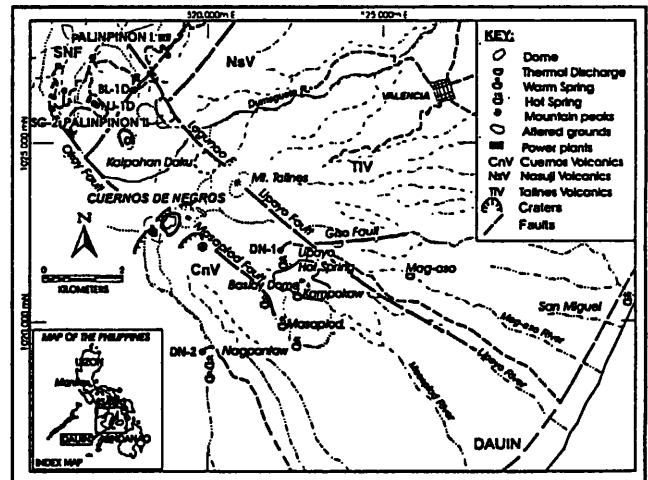


Figure 1. Location map of the Dauin Geothermal Prospect, thermal springs, and exploratory wells DN-1 and DN-2. The Palinpinon Field is also shown northwest of the area.

Table 1. Water Chemistry of Baslay-Dauin Thermal Areas

Sample Code	Sample Date	Flow (kg/s)	Temp. (°C)	pH	Na	K	Li	Ca	Mg	Cl	SO ₄	HCO ₃	tCO ₂	H ₂ S	B	SiO ₂	NH ₃
					Concentration in mg/L												
San Miguel	10/16/81	1.2	87.0	2.16	119	11.2	0.2	235	54.7	993	220	0	217	0	4.9	296	2.7
Lipayo #2	12/29/81	0.50	48.0	6.70	48	8.1	0.04	74	29.8	75	87	na	nd	nd	0.71	137	0.70
	05/18/82	0.76	46.5	6.18	50	8.6	0.04	82	30.6	11	90	na	561	0.65	2.24	150	0.22
	12/12/82	1.06	46.0	6.48	51	7.9	0.04	84	30.0	nd	97	na	nd	nd	1.78	162	0.14
	07/04/89	nd	42.0	6.07	47	9.0	0.04	88	31.2	56	89	329	621	0.17	0.56	141	0.23
	10/12/94	0.70	45.0	7.67	45	11.4	nd	64	85.0	111	208	308	229	nd	1.94	170	nd
	05/25/96	0.94	47.0	3.51	51	10.2	nd	76	28.0	113	860	nd	178	nd	0.10	154	0.10
	10/27/96	0.94	44.0	6.16	nd	15.5	nd	73	27.8	70	160	84	279	0.68	0.49	152	0.04
Lipayo #3	05/25/96	nd	32.0	3.21	16	5.4	nd	32	9.0	28	100	0.00	321	0.00	0.32	111	0.24
	10/27/96	nd	30.0	5.57	nd	6.0	nd	34.5	8.4	14	180	73.69	297	0.68	0.43	113	0.63
Masaplod #3	12/29/81	8.82	61.1	2.01	93	29.9	0.1	38	26.8	603	1659	na	176	7.49	6.99	190	0.54
	05/18/82	12.50	59.5	1.61	93	30.5	0.1	35	30.5	656	1817	na	229	6.07	0.27	181	0.66
	12/12/82	15.80	60.0	2.07	96	30.7	0.1	82	31.1	646	1761	na	na	nd	7.12	204	na
	07/26/89	nd	60.0	1.97	94	27.4	0.1	110	31.8	402	851	na	15	0.34	4.75	204	na
	10/27/94	4.50	61.0	2.47	100	36.4	nd	98	84.6	515	1440	na	na	nd	5.94	214	0.18
	05/26/96	4.50	62.0	1.97	101	28.9	nd	82	30.5	599	300	na	na	nd	5.84	192	1.88
	10/27/96	4.70	60.0	1.96	96	25.0	nd	76	31.0	561	1460	na	na	0.68	5.16	193	
Campokaw-3	09/18/81	0.81	33.6	7.58	61	12.8	0.1	93	56.0	192	196	329	12	9.80	1.64	137	0.81
	06/01/96			7.88	13	4.8	0.0	22	11.0	28	60	1.89	86	nd	0.38	90	0.03

N.B. Data was after Glover, 1975; Harper and Arevalo, 1982; and Mejorada, 1996. (nd - no data; na - no analysis).

Surface Thermal Manifestations and Water Chemistry

Impressive surface thermal manifestations in Baslay-Dauin consist of warm springs, hot springs, steaming grounds, hydrothermally altered ground and bubbling mud pools. These thermal features cover an area of about 50 km² (Harper and Arevalo, 1982) of the southern part of Cuernos de Negros (Figure 1).

The water chemistry of selected thermal discharges is summarised in Table 1 together with new data collected in 1996.

A ternary plot of the anionic constituents of the springs is given in Figure 2. As shown, the surface chemistry of the Dauin thermal springs consists of acidic chloride-sulphate and dilute

neutral chloride-bicarbonate water with pH of 1.6 (e.g., Masaplod) to 7.8 (i.e., Campokaw). The chemistry of the springs indicates that they are mostly secondary springs that are formed and controlled by near-surface processes. None of the springs plot within the neutral-pH NaCl waters or the "matured water" apex suggesting the lack of waters of direct discharge from the resource. Hence, geothermometric estimates using solute geothermometers are meaningless. The spring flowrates range from .50 kg/s to 15.8 kg/s (e.g., Masaplod) and surface temperatures range from 30 to 87°C. Masaplod and San Miguel springs define a dilution trend along the volcanic-water side and exhibit the highest chloride and temperature but are acid and typically contain native sulphur in their discharge path (Glover, 1975).

Figure 3 shows the enthalpy-chloride diagram of the Dauin thermal discharges. Assuming that DN-1 fluid represents the parent fluid, then several processes may be inferred to understand the origin of the springs. Line A indicates that Lipayo 1 was produced by mixing of steam condensate with geothermal brine. Line B defines a simple dilution of DN-1 fluid and ground water forming the San Miguel and the Masaplod 1 and 2 springs. In contrast, Line C in the diagram indicates steam heating of Nagpantaw and Lipayo waters corresponding to increased enthalpy values with no appreciable changes in their chloride concentration. Line D, however, suggests mixing of steam-heated ground water with geothermal brine as defined by Lipayo 1, Masaplod 1 and Masaplod 2 waters.

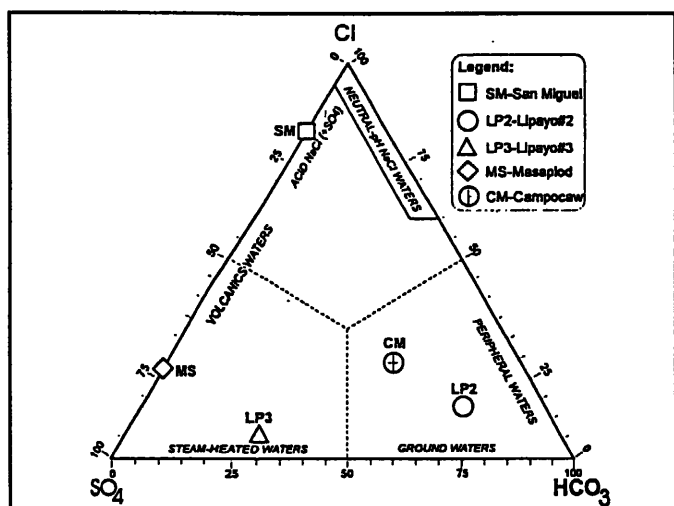


Figure 2. Ternary plot of Dauin springs.

Source of Sulphur

The presence of native sulphur in the discharge of DN-1 has provoked much speculation and debate about its depth of origin

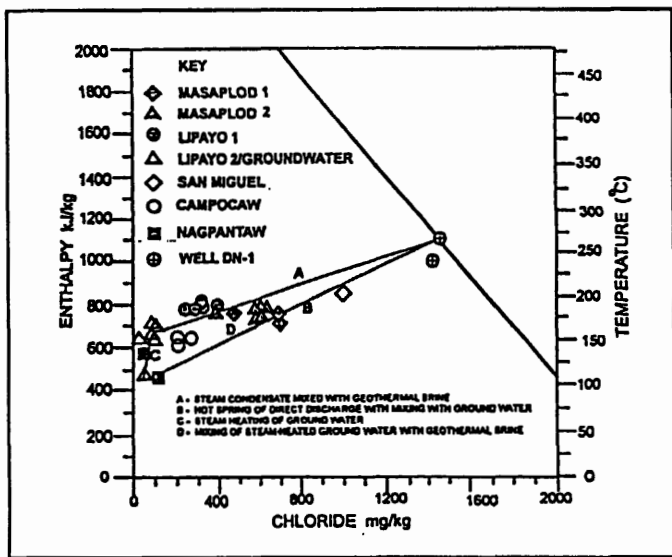


Figure 3. Chloride-enthalpy plot of Dauin springs and well DN-1. The relative location of the springs and samples is given in Figure 1.

and genesis. The issue has been made more interesting by the fact that the accompanying discharge fluid remained neutral (pH 6.40 to 7.20) throughout the initial discharge since fluid in contact with native sulphur will turn acidic at equilibrium conditions.

Two views on the possible source location of sulphur at DN-1 are reviewed in this paper: 1) from the blind-drilled section, 2,230 to 2,623 m, Reyes, 1983; and 2) from a possible cas-

ing break between 850 to 930 m (Hermoso, 1996). Figure 4 illustrates the location of the possible source of sulphur in DN-1 and the other salient data pertinent to the review.

The speculation that sulphur could have originated from the blind-drilled section between 2,230 and 2623 is premised on the following:

- 1) The absence of sample from the blind-drilled section (2,230 to 2,623 m).
- 2) The highest H₂S levels detected at 2,450 m during downhole sampling.
- 3) The "H₂S-reeking" core 7 taken from 2,217 m, about 23 m from the total loss zone where blind-drilling began.

The second speculation on the depth of origin infers a possible casing break between 850 to 930 m (Hermoso, 1996). The strong evidences for this speculation are:

- 1) The presence of discrete acid alteration minerals between the postulated depth which included alunite and natroalunite, sulphur, quartz, pyrite and rutile (Reyes, 1983 and Villarosa, 1994).
- 2) The preponderance of acid alteration between 200 to 1,200 m pointing to the most likely source as the cased-off and cemented section.
- 3) All samples from 1,307 to 2,623m including smectite, illite, chlorite, quartz, epidote, calcite and zeolite suggest the passage of neutral-pH within the said section.

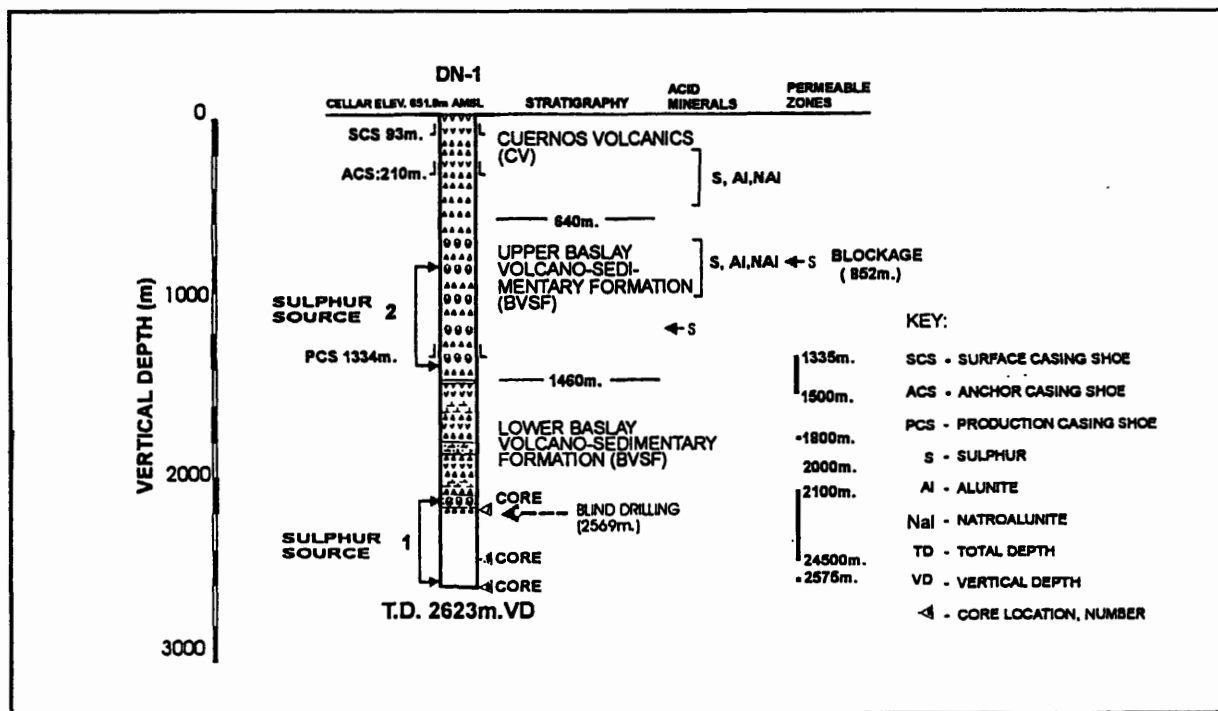


Figure 4. Illustrates the location of the possible source of sulphur in DN-1 and the other salient data pertinent to the review.

- 4) Sulphur when present in abundance is highly corrosive to casing and cement as was experienced in Rotokawa, New Zealand (Truesdell, pers. Comm., 1996).
- 5) The presence of blockage at 851 m and the composition of the blockage (mainly cement and alunitized chips, Villarosa, 1994) was interpreted to be a possible casing break.

The first argument on the source depth of sulphur appeared to be based on negative evidence rather than the physical presence of sulphur. The sample that reeked of hydrogen sulphide, however confirmed the high H₂S level within the well but does not pinpoint specific depth location since this can be assimilated by the sample during sample retrieval. The presence of high H₂S level at 2450m from the downhole sample suggests that sulphur is present at depth in the form of sulphur species H₂S but in no way identify any definitive depth of origin since downhole samples from newly drilled wells do not necessarily reflect stable well condition and are prone to subjective speculation.

The second argument and facts appear to provide better explanation for the source depth of sulphur and give tangible evidence compared with the former. This argument is corroborated by petrologic evidences and recent downhole surveys. It is argued here that the blockage at 850 m is due to a casing break caused by the corrosive fluid at such depth. The presence of alunitized cement chips strongly argued for the casing break. Alunite, (K, Na) Al₃(SO₄)₂(OH)₆, when found as fresh euhedral crystals together with pyrite, quartz, and sulphur has been used as positive indicator for the presence of acid fluids in Philippine geothermal wells (Reyes, 1990). Since no alunite mineral was found in the well except from 850 to 930 m would support the casing break theory and that sulphur entered the well either as a result of corrosion or from casing implosion.

There are some doubts, however, on when the break occurred due to the absence of evidence for a casing break prior to the discharge and even a day prior to the shutting of the well. In fact, on May 30, 1983 the downhole survey tool reached 2,600 m (Harper and Clotworthy, 1983). The apparent difficulty in the initial attempt to conduct downhole surveys was interpreted to be due to high mass flow conditions (>25 kg/s) rather than due to blockage in the well. Thus, this would imply a depth source behind the casing with entry at 1,350 m immediately below the production casing. Conversely, the fact the the survey tool is only 32 mm in diameter would similarly indicate that the blockage could not have been detected during the lowering of the instrument and only the 60 mm diameter "Go-devil" survey can detect it. The fact that alunitized cement chips were recovered from the 40 mm impression block would suggest the source being mainly from the cased-off section. Furthermore, the amount of sulphur discharge in the well never diminished would suggest a continuous replenishment within the well that is accompanied by notable change in colour of the weirbox fluid from dark green to dark grey at throttled conditions.

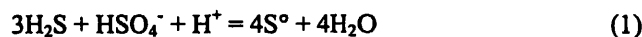
Thus, based on the DN-1 limited discharge the presence of discrete sulphur feed entering the well is inferred. This feed

mixes with the neutral fluid. However, it seems the contact time was insufficient to produce an acid fluid.

Genesis of Sulphur at DN-1

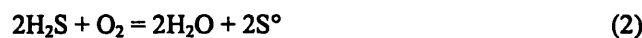
The other question in the prospect area is the possible genesis of sulphur abundantly discharged at the weirbox. The sulphur can be coming from depth (as molten sulphur) or generated at the surface.

Several mechanisms for the formation of elemental sulphur have been invoked. Harper and Clotworthy (1983) suggested that the sulphur could form from the reservoir fluid from the following reaction:

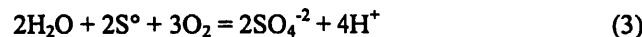


This seems unlikely as the well discharged neutral waters, belying the presence of acidic reservoir fluids sufficient to generate the high amounts of sulphur at the weirbox.

However, the discharge fluids have very high H₂S levels (200 times the neutral wells in Palinpinon). In this case, elemental S can easily be generated at the weirbox from the surface oxidation:

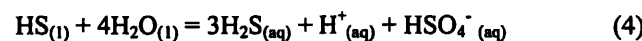


The complete sulphide oxidation process from equation 2 can be described by:



Although reaction 3 is thermodynamically favoured at the weirbox, it is kinetically inhibited and needs to be catalyzed by sulphur-oxidizing bacterium. It is for this reason that sulphide oxidation is not completed to produce the acid sulphate waters but is arrested until S formation only (Ellis and Giggensbach, 1971).

The other possibility forwarded is that the S is entering the well in its molten phase (melting point = 115°C) at depth (e.g., from the casing break at 850 m) and below or flowing behind the casing and entering at 1,350 m) and solidifies upon cooling at the weirbox. Sulphur hydrolysis is expected to occur once molten sulphur is in contact with water at high temperature as expressed by the reaction:



Thus, acidic sulphate waters are expected at the surface discharge. This equation is favoured at high temperatures producing very high H₂S gas output. The neutral discharge of DN-1 suggests that active S hydrolysis is not occurring during the discharge testing. The very high H₂S levels in the discharge would suggest reaction 4 occurring at some discrete points of the reservoir (e.g., presence of buried S bodies at shallow depths), with the acidic waters produced already effectively neutralised by the reservoir rocks (Truesdell, Pers. Comm., 1996). Thus, only the neutral high H₂S waters reach the surface where partial H₂S oxidation (reaction 2) produces the elemental S at the weirbox.

From the above discussions, debates were similarly focused on whether sulphur produced the H_2S by hydrolysis (shallow, non-magmatic source) or whether H_2S at depth as suggested above, produced the sulphur (magmatic source).

The only available data on the isotopic composition of the elemental sulphur from DN-1 indicate $\delta^{34}S$ value of -4‰ indicative of the kinetic fractionation during formation by oxidation of H_2S with $\delta^{34}S$ of around zero ‰ (Robinson, et al., 1987). This favours the formation of sulphur at shallow depth and the kinetic fractionation explains the neutral-pH of DN-1 discharge.

The Dauin Potential and Future Strategy

From the foregoing discussions we have examined the options for further works at Baslay-Dauin. Two options are identified: 1) work-over of DN-1 and 2) drill a new well, DN-3D (Candelaria, 1994, Bayrante, 1996).

The former option involves the assessment and verification of the casings and liner including the repair of any casing breaks below 850m. Dowhole surveys and sampling at shut and open conditions are envisioned to better characterise the feed zones following the work-over. The data from these activities are intended to verify and locate the extent of the sulphur intersected by the well that contribute directly to the discharge. The data will also be useful in assessing future drilling targets.

The latter option, on the other hand, requires the drilling of a third well in the prospect either from the same pad as DN-1 or distant from it. The proposed well, DN-3D, is intended to gather more information at the northeast sector and at the same time address outstanding issues constrained by the present paucity of data.

Between the two options, it is recommended here that drilling of the third well, DN-3D, be pursued first using a new pad. Likewise, we recommend the subsequent mechanical work-over of DN-1. This exploration tack is intended not only to better characterise the prospect but also to address any environmental issues attendant to future testing since DN-1 can be ini-

tially used as an injection well. No further work is recommended at present until after the exhaustive testing and evaluation of Baslay-Dauin after the proposed drilling.

Conclusion

Based from the discussion above there are two postulated source location of sulphur at DN-1: 1) between 2,230 to 2,623 m, the blind-drilled section and 2) between 850 to 930 m, a possible casing break. This study favors the second postulate based on the available evidences from drilling, petrology, and down-hole surveys. The first postulate, although cannot be ruled out, appears bereft of evidences but suggests that sulphur is present at depth in the form of H_2S .

The sulphur in DN-1 discharge fluid is interpreted here to have been formed at the surface from the partial oxidation of H_2S derived from the neutralised fluid from hydrolysis of sulphur beds distant from DN-1. This study argues for the likely presence of a neutral-pH exploitable resource close to DN-1 (Figure 5).

The geothermal areas similar to Dauin are the Rotokawa, New Zealand and the Tatun, N. Taiwan that are in the advanced stage of deep drilling. At Rotokawa, sulphur containing beds occur at depths of about 100 meters. Deep drill holes (300 to 1,200 m) tapped 200 to 250°C, neutral pH, dilute alkali-Cl waters, with the rising geothermal waters encountering sulphur beds at shallow depths produced the acidic (pH = 2.1 to 2.5), high sulphate (500-1000 mg/kg) spring waters associated with high H_2S output (Ellis and Giggenbach, 1971; Krupp and Seaward, 1987).

Acknowledgment

We thank the management of the Philippine National Oil Company-Energy Development Corporation for allowing us to publish this report. R.M. Abiera, L.M. Respecia, and J.L. Ballo-allo helped in assembling the final draft of this paper.

References

- Bayrante, L.F., 1996. Proposed Development Drilling Strategy, Dauin Geothermal Prospect, Negros Oriental, *PNOC-EDC Int. Rpt.*, 5 p.
- Candelaria, M.N.R. 1994. Dauin Development Strategy. *PNOC-EDC Int. Rpt.*, 5 p.
- Ellis, A.J. and W. Giggenbach, 1971. Hydrogen Sulphide Ionization and Sulphur Hydrolysis in High Temperature Solution. *Geochimica et Cosmochimica Acta*, vol. 35, p. 247 to 260.
- Glover, R.B., 1975. Chemical Analyses of Waters From Negros Oriental, Philippines and Their Geothermal Significance. Chem. Div., D.S.I.R., New Zealand.
- Gonzales, R.C.; 1983. Dauin-1 Well Data. *PNOC-EDC Int. Rpt.*
- Gonzales, R.C., 1983. Dauin-2 Well Data. *PNOC-EDC Int. Rpt.*
- Harper, R.T. and E.M. Arevalo, 1982. A Geoscientific Evaluation of The Baslay-Dauin Prospect, Negros Oriental, Philippines. *Proceedings of the Pacific Geothermal Conference and 4th New Zealand Geothermal Workshop.*
- Harper, R.T. and A.W. Clotworthy 1993. Evaluation of DN-1 Discharge Data (data to date); Recommendations for Future Work and Comments, Recommendation for DN-2. KRTA and *PNOC-EDC Int. Rpt.*, 11 p.

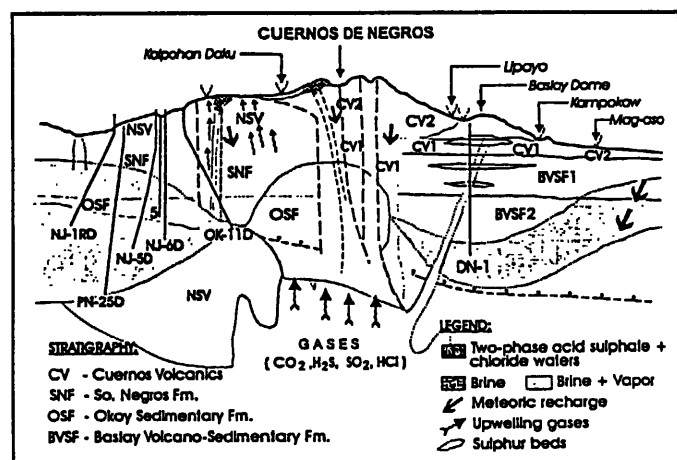


Figure 5. A north-south section of the Palinpinon geothermal field and the Dauin geothermal prospect illustrating a hypothetical model of the resources.

- Hermoso, D.Z.(ed.), Reyes, A. G. and R.C. Gonzales, 1989. Well DN-1 Geologic Report, Baslay-Dauin, Southern Negros Geothermal Project. *PNOC-EDC Int. Rpt.*, 46 p.
- Hermoso, D.Z.(ed.), Reyes, A.G. and R.C. Gonzales, 1989. Well DN-2 Geologic Report, Baslay-Dauin, Southern Negros Geothermal Project. *PNOC-EDC Int. Rpt.*, 16 p.
- Krupp, R.E. and T.M. Seward, 1987. The Rotokawa Geothermal System, New Zealand: an Active Epithermal Gold-Depositing Environment. *Economic Geology and the Bulletin of the Society of Economic Geologists*, vol. 82, no. 5, p. 1109-1129.
- Pamatian, P.I., 1992. Surface Structures and Related Thermal Features in the South Laguna and Baslay-Dauin Sectors. *PNOC-EDC Int. Rpt.*
- Reyes, A.G., 1983. Petrology of Well Dauin-1 (revised), Baslay-Dauin, Southern Negros Geothermal Project. *PNOC-EDC Int. Rpt.*, 12 p.
- Reyes, A.G., 1983. Petrology of Well Dauin 2, Baslay-Dauin, Southern Negros Geothermal Project. *PNOC-EDC Int. Rpt.*, 10 p.
- Reyes, A.G. , 1990. Petrology of Philippine Geothermal Systems and the Application of Alteration Mineralogy in their Assessment. *J. Volcanol. Geotherm. Res.*, 43, p 279-309.
- Robinson, B.W., Villasenor, L.B. and Clemente, V.C., 1987. Preliminary Stable Isotope Investigations of Acid Fluids in Geothermal Systems in the Philippines. *Proceedings of the 9th New Zealand Geothermal Workshop*, Auckland, New Zealand, p. 73-78.
- Truesdell, A.H., 1996. Report of the April 1996 Visit of A.H. Truesdell to the PNOC Geothermal Fields. *PNOC-EDC Int. Rpt.*, 6 p.
- Villarosa, H.G.A., 1994. "DN-1 Impression Sample Petrologic Report." *PNOC-EDC Int. Rpt.*