

## Geochemical Modeling of Thermal Springs in Colombia

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**Keywords:** Geochemical modeling, activity coefficient, equilibrium temperature, saturation index, Azufral, Paipa, Cundinamarca.

### ABSTRACT

A preliminary geochemical modeling of Azufral and Paipa geothermal systems, and the N-NE area of Cundinamarca District (Republic of Colombia), was carried out; based on chemical analyses from the most remarkable thermal springs by using *GWB* software. Activity coefficients were obtained by the Debye-Huckel approach and virial methods according to sample salinity. The estimated temperatures were as follows. (1) The fluid equilibrium temperature for El Batán, the hottest spring water in Paipa (75.5°C), although equilibrium with chalcedony phase was about 100°C, while the calculated saturation indices suggested an equilibrium temperature of 107°C. For most of Paipa's samples, anhydrite was found supersaturated above 90°C. (2) Most Azufral samples have an equilibrium temperature between about 57°C and slightly above 200°C. The fluid's equilibrium temperature with quartz, for seven thermal springs in Azufral geothermal system, varies between 166 and about 200°C. (3) Cundinamarca District, whose highest sampling temperature was 50.8°C, showed lower equilibrium temperature, which was not higher than 93°C. As modelling was performed using spring data, it is possible that higher temperatures occurred at depth since hot waters are affected by cooling processes such as mixing with cooler waters when ascending to the surface. However, the results obtained indicated the presence of medium temperature geothermal resources in Colombia and allowed a preliminary identification of the most interesting zones.



**Figure 1:** Location map of Azufral and Paipa geothermal systems, and Cundinamarca Province in Colombia, South America.

### 1. INTRODUCTION

Colombia is a country with a great geothermal potential. Nevertheless, it does not take any advantage of that situation because of the lack of sufficient economic resources for detailed exploration.

To advance in the geochemical characterization, a sampling of the superficial springs has been undertaken in three areas, which correspond to the geothermal systems of Paipa and Azufral, and the northern and northeastern sectors of Cundinamarca Province (Figure 1). Azufral Geothermal System shows potential for electric energy generation in the Nariño Province, and was classified as a medium to high enthalpy system (Alfaro, 2001); Paipa Geothermal System has a complexity because of a high salinity in its subsurface and is under evaluation at the moment to determine its suitable use; while Cundinamarca Province offers some alternatives for direct uses.

The purpose of this preliminary geochemical modeling is to estimate the fluid equilibrium temperature for the springs and establish their chemical equilibria under subsurface conditions. Also, it is the purpose of the work, to obtain a preliminary idea about reservoir conditions. Data were provided by *INGEOMINAS* (Colombian Geological Survey).

### Methodology

The sampling was carried out between 2001 and 2002. 42 spring samples were collected: 19 from Paipa Geothermal Area, 15 from Cundinamarca Province, and eight from Azufral Geothermal Area.

As for the sampling methodology, it was performed according to the standard procedure (Giggenbach and Goguel, 1989; Arnorsson, 2000). Two different samples were collected from every spring and bottled in plastic flasks (Alfaro, 2002): 500 ml of filtered and acidified with  $\text{HNO}_3$  for cations, B and  $\text{SiO}_2$  analyses; and 500 ml of untreated sample for conductivity, pH, bicarbonate, chloride and sulfate analyses. The chemical composition of the samples is shown in Table 1.

Table 2 shows the estimation of reservoir temperatures according to the Cationic Composition Geothermometer (TCCG) (Nieva and Nieva, 1987), which serves as a reference with regard to the temperatures obtained for subsurface conditions; related with the springs. The TCCG is a very useful tool, since it employs the concentrations of the main cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ ), which makes it very accurate (it is neither optimistic nor pessimistic) in comparison with other cation geothermometers and silica geothermometers. As is shown in the same table, silica geothermometers (Fournier and Potter II (1982); Giggenbach (1991); and Fournier (1973)) were also calculated.

**Table 2. Reservoir temperatures estimated by silica and cation geothermometers.**

Sample	T (no-steam loss) (°C)	T spring disch. (G) (°C)	TCCG (°C)
Paipa			
BP	123.2	102.4	228.2
PA	113.7	91.3	212.7
PI	108.9	85.7	219
MI	112.1	89.5	221.5
HL	113.7	91.3	213.6
OD	116.4	94.4	224.3
P2	48.0	17.9	217
O	136.4	118.1	36
ML	113.9	91.6	223.5
PM	81.6	54.7	207
PS	93.6	68.3	222.3
EE	41.5	10.9	32.8
SA	34.5	3.4	26.9
E2	107.2	83.8	222.3
BI	107.2	83.8	42
Cundinamarca			
N	70.8	42.7	236.6
V1	89.3	63.4	45.9
AC	60.3	31.2	174.7
R	48.8	18.7	209.8
PC	95.9	70.9	137.9
PT	101.0	76.6	148.7
VP	79.5	52.4	120.7
EZ	98.9	74.3	126.9
AT	97.3	72.4	128.0
BA	56.4	26.9	176.0
LL	64.6	35.9	190.6
SO	73.8	46.0	86.9
MO	68.8	40.5	214.7
V2	77.0	49.6	173.8
SM	87.6	61.4	181.2
Azufra			
T1	184.7	177.5	193.1
QB	177.5	168.4	186.5
LV	183.3	175.7	201.9
MA	158.4	144.7	193.5
LC	133.9	115.1	199.9
SR	159.4	145.9	183.6
TE	146.6	130.3	177.1

## 2. GEOCHEMICAL MODELING

Geochemical reaction modeling was based on the Geochemist's Workbench (GWB) (Bethke, 1994) software, by using React and Gtplot programs. This program employs an approach of some variations of Debye-Hückel and virial methods for estimating activity coefficients and temperatures at which some minerals are equilibrated in the subsurface, starting from analytic concentrations of the solutes and the pH's. For each value of temperature, a chemical composition of the fluid and the saturation index of the minerals were obtained. The saturation index (SI) is the ratio between the mineral's activity product (Q) and the equilibrium constant (K), according to the following equation:

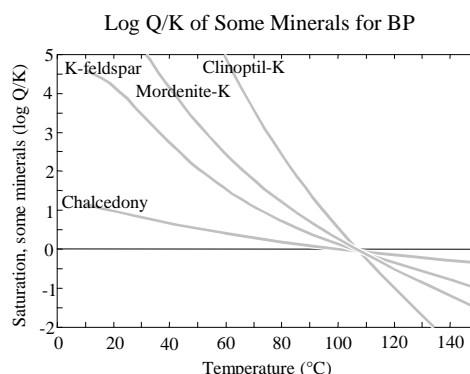
$$SI_1 = \log Q_1 - \log K_1 = \log (Q_1/K_1)$$

The aluminum concentration was assumed for all the samples, with a value of 0.001 ppm; because of the chemical analyses are incomplete. All the samples used in the plots are around neutral pH.

## 3. RESULTS

With regard to Paipa Geothermal System, Alfaro (2002) applied the SOLVEQ Chemical Model to the same samples and the equilibrium temperatures were almost the same than the ones obtained by using GWB software; especially with regard to quartz and anhydrite.

Figure 2 shows an equilibrium temperature of around 107°C with K-feldspar, chalcedony, mordenite-K and clinoptil-K (zeolite). Sampling temperature is 75.5°C and predicted equilibrium temperature is around 107°C. The estimated temperature for the reservoir was 228°C, by using TCCG; and 123.2°C, by using silica geothermometer (no-steam loss).

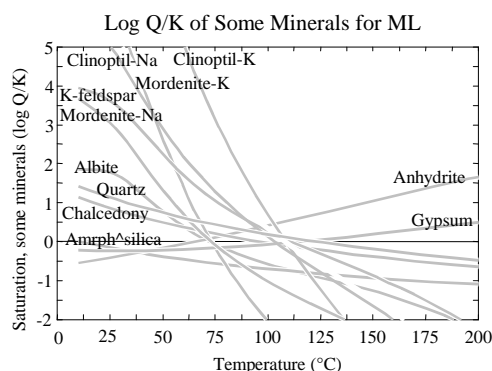


**Figure 2. Calculated saturation indices (log Q/K) of some minerals plotted versus temperature for the spring Batán (BP) from Paipa Geothermal System.**

As can be seen, there are marked differences among the equilibrium temperature and the temperatures estimated by using cation and silica geothermometers. The cause of this difference is a mixing process, which is affecting the ascending hot fluid. Aguirre (2003) estimated the composition of the hot member for Paipa Geothermal System, based on the sample BP, and obtained a temperature of 174.5°C for reservoir conditions.

Alfaro (2002) obtained several equilibrium temperatures and the highest one between 200 and 240°C, whose mineral assemblages are composed by Mg, Ca and Fe silicates, and Mg oxide and carbonate. The quartz – anhydrite assembly seems to occur at about 120°C.

According to Figure 3, there are several equilibrium temperatures; which are in the range 72°C to 120°C (gypsum – quartz assembly). The estimated temperature for the reservoir was about 223°C, by using TCCG; and 113.9°C, by using no-steam loss geothermometer.

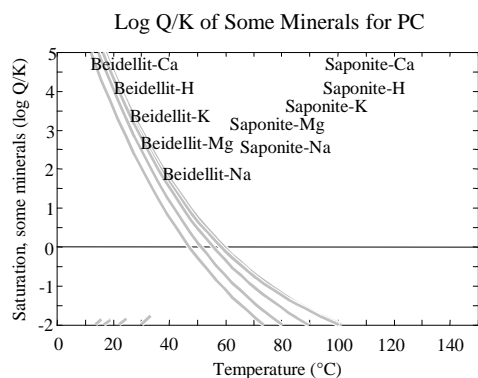


**Figure 3. Calculated saturation indices (log Q/K) of some minerals plotted versus temperature for the sample Motobomba Lanceros (ML) from Paipa Geothermal System.**

In summary, for Paipa Geothermal System; mordenite-K, clinoptil-K, K-feldspar, chalcedony and quartz are

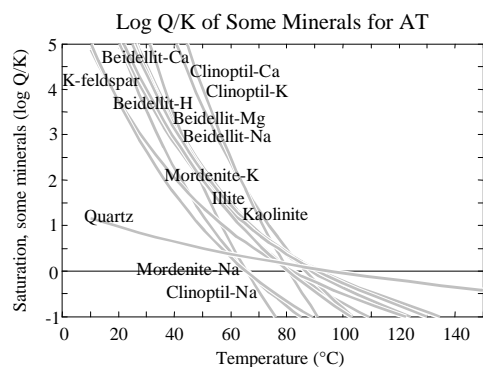
supersaturated at surface, while gypsum and anhydrite are under-saturated.

As can be seen in Figure 4, the sample PC shows an equilibrium temperature of about 52°C with two types of smectite (beidellit and saponite). Beidellit minerals are supersaturated below this temperature, whereas saponite minerals are supersaturated above it. The sampling temperature is 43.3°C. All the silica geothermometer values for this sample were higher than the equilibrium temperature seen on this diagram.



**Figure 4. Calculated saturation indices (log Q/K) of some minerals plotted versus temperature for the spring Paraiso CODECAL (PC) from Cundinamarca Province**

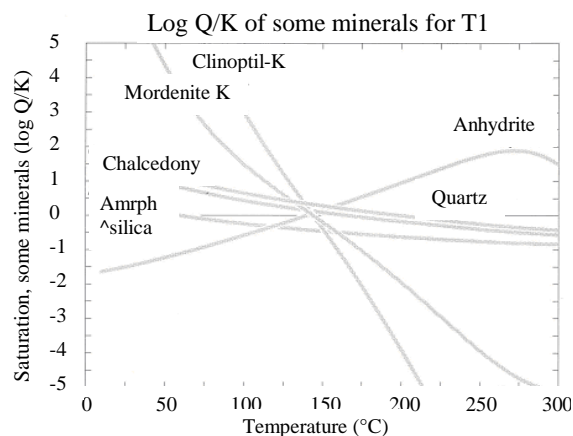
According to Figure 5, the equilibrium temperature ranges from 65 to 93°C. The sampling temperature is 37.1°C and the estimated temperature for the reservoir is 128°C, by using TCCG; and 97.3, by using quartz geothermometer (no-steam loss). The assemblages involve clinoptil (zeolite), beidellits (smectites), K-feldspar and quartz. Most of these minerals are supersaturated below 93°C.



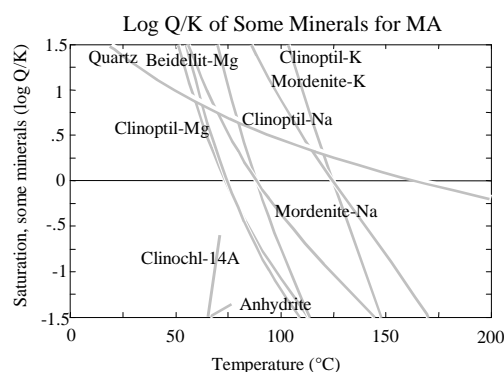
**Figure 5. Calculated saturation indices (log Q/K) of some minerals plotted versus temperature for the spring Aguas Calientes 3 (AC) from Cundinamarca Province.**

As is shown in Figure 6, quartz is at equilibrium at around 190°C. The estimated temperature for the reservoir is 184.7°C, by using quartz geothermometer (no-steam loss); and 193°C, by using TCCG. The main assembly involves clinoptil-K, mordenite-K and anhydrite.

It can be seen from Figure 7 that there are several equilibrium temperatures, which range from 75 to 172°C. The estimated temperature for the reservoir is 193.4°C, by using TCCG; and 158.4°C, by using quartz geothermometer (no-steam loss). The highest temperature corresponds to the quartz – anhydrite assembly.



**Figure 6. Calculated saturation indices (log Q/K) of some minerals plotted versus temperature for the spring Tercan 1 (T1) from Azufral Geothermal System. Sampling temperature is 47°C.**



**Figure 7. Calculated saturation indices (log Q/K) of some minerals plotted versus temperature for the spring Malaver (MA) from Azufral Geothermal System.**

Most of the samples reflect the latter equilibrium temperature, which are the lowest on the plots. The highest equilibrium temperatures on the plots are similar to the ones obtained from silica geothermometers.

Since all of the samples correspond to thermal springs, they would mainly be affected by degassing and mixing processes, which would imply a great complexity for establishing their evolutionary histories (Pang and Reed, 1998).

Anhydrite is supersaturated under reservoir conditions in Paipa and Azufral geothermal systems.

## CONCLUSIONS

Equilibrium temperatures of Paipa Geothermal System based on mineral assemblages ranged from 70 to 125°C. The fluid's equilibrium temperature for El Batán (BP), which is the hottest spring, is about 107°C. For most of samples, anhydrite was found supersaturated above 90°C. However, this equilibrium temperature is much lower than that estimated by geothermometry, which is caused by a mixing process between deep hot waters and shallower waters.

Most of Azufral's samples have an equilibrium temperature between 57°C and slightly above 200°C. The fluid's equilibrium temperature with quartz, for seven thermal springs in Azufral Geothermal System, varies between 166 and about 200°C.

Cundinamarca Province, whose highest sampling temperature was 50.8°C, showed lower equilibrium temperature, which was not higher than 93°C.

Since most of the samples correspond to thermal springs, they are affected by degassing and mixing processes when coming out to the surface, and reflect the latter equilibrium temperature.

#### ACKNOWLEDGEMENTS

The authors are very grateful with INGEOMINAS, IAEA and Instituto de Investigaciones Electricas – IIE (Mexico) for their invaluable support.

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**Table 1. Chemical composition (in mg/kg) of thermal springs from Paipa and Azufral geothermal systems, and Cundinamarca Province.**

Sample	Location	t (°C)	pH	Li	Na	K	Mg	Ca	B	SiO <sub>2</sub>	F	Cl	SO <sub>4</sub>	HCO <sub>3</sub>
Paipa Geothermal System														
BP	Batán	75,5	7,4	10,60	5500	725	22,5	100	2,4	77	18,7	2378	8250	1420
PA	Pozo Azul	53,7	7,0	18,00	13525	1500	18,0	90	5,2	64	15,2	5351	20187	2700
PI	Pozo Inundado	43,5	7,3	18,00	11750	1400	17,0	77	5,3	58	14,0	4890	19687	2475
MI	M. P. Inundado	52,7	6,8	18,00	12250	1500	18,0	77	4,8	62	14,8	5253	19750	2580
HL	Pozo H. Lanceros	63,4	7,2	18,00	12500	1400	17,0	87	4,9	64	14,7	5138	19375	2520
OD	Ojo del Diablo	68,1	7,0	18,20	12375	1562	21,2	175	5,1	68	15,5	5103	19250	2606
PB	Pozo Blanco	62,2	7,0	20,00	13000	1500	17,0	100	4,9	64	15,3	5333	20937	2640
P1	Piscina Olímpica	25,1	6,0	3,40	2450	280	10,0	48	0,1	15	0,3	1154	4187	479
P2	Piscina Olímpica	25,9	6,1	2,20	1975	230	10,0	50	0,6	13	0,1	985	3050	373
O	Olitas	23,2	5,7	0,10	24	15	0,9	12	0,0	99	3,2	1	18	94
ML	Motob. H.Lanceros	69,8	7,1	18,10	12375	1550	22,5	175	5,1	64	15,3	5065	19812	2606
PM	Las Marismas	21,5	6,3	22,90	16926	1757	14,6	47	7,4	32	5,8	7095	26652	2989
PS	Salpa	21,0	6,5	18,00	13250	1637	22,5	175	5,3	42	6,1	5455	20812	2620
PC	Pozo Cascajera	19,2	5,8	0,20	195	20	67,5	200	0,1	17	0,1	116	1100	47
EE	Esc. La Esperanza	21,5	5,6	0,10	290	25	42,5	250	0,1	11	0,1	168	1150	23
LP	Finca La Puebla	14,8	4,9	0,10	1	1	0,4	1	0,1	9	0,0	2	1	2
SA	Finca San Antonio	16,5	6,3	0,10	14	4	1,0	8	0,1	9	0,2	10	1	63
E2	Erika	53,2	6,7	1,30	445	55	8,5	70	0,5	56	1,8	639	6	603
BI	El Batán	56,0	6,8	0,40	105	20	4,0	20	0,3	56	0,7	55	2	310
Cundinamarca Province														
N	Nápoles	46,7	7,3	0,02	10	4	2,1	7	0,2	24	0,1	1	6	64
V1	Volcanes M.	53,7	7,7	0,01	6	2	4,4	31	0,2	38	0,3	2	3	135
AC	Agua Clara	33,2	6,8	0,04	3	1	0,4	4	0,2	18	0,3	0	2	18
R	Repetidora	22,2	6,6	0,01	2	1	0,3	2	0,2	13	0,1	0	2	12
PC	Paraiso Codecal	43,3	7,4	0,01	365	8	5,8	98	0,8	44	0,5	597	0	337
PT	Paraiso Termal	50,8	7,5	0,01	203	6	4,3	51	0,4	49	0,5	256	0	340
VP	Vereda Peñas	36,8	7,9	0,08	209	3	2,1	7	0,5	30	1,0	97	0	450
EZ	El Zipa	50,0	8,1	0,02	532	7	3,7	47	0,1	47	0,5	793	2	225
AT	Aguas Calientes 3	37,1	7,6	0,09	465	6	3,7	45	0,2	45	0,5	698	5	195
BA	Bavaria	31,1	7,1	0,03	19	2	1,3	10	0,2	17	0,4	15	7	61
LL	Los Lagartos	36,0	7,3	0,01	33	4	2,8	15	0,2	21	0,3	9	0	143
SO	Soratama	27,1	8,0	0,00	2600	6	8,0	46	0,2	26	0,9	3930	9	284
MO	Montecillo	39,0	7,4	0,08	8	2	1,4	8	0,2	23	0,3	8	3	42
V2	Volcanes Choachí	35,0	7,7	0,06	80	8	17,0	74	0,2	28	0,6	61	51	395
SM	Santa Mónica	50,2	7,8	0,02	67	7	6,8	49	0,2	36	0,6	45	3	326
Azufral Geothermal System														
T1	Tercán 1	47	6,4	1,80	650	73	305,0	277	10,7	214	0,1	1402	185	1669
T2	Tercán 2	41	6,6	1,80	675	73	300,0	290	12,5	212	0,0	1402	195	1669
QB	Quebrada Blanca	47,3	6,3	1,20	474	38	49,0	87	5,7	193	0,0	763	145	381
LV	Laguna Verde	49,4	6,2	0,20	87	14	15,5	52	0,5	210	0,1	26	125	256
MA	Malaver	29,7	6,6	2,40	1412	123	305,0	167	21,2	144	0,1	2023	147	2430
LC	La Cabaña	23,2	6,7	0,10	15	4	10,7	12	0,1	94	0,0	5	1	140
SR	San Ramón	28,3	6,3	0,60	439	40	129,0	76	6,1	146	0,2	568	20	1215
TE	Tenguetán	17,8	6,2	1,40	627	50	272,0	240	8,2	118	0,0	1420	62	1464