

2.1. Introduction

The thermal springs are natural geological phenomena and are described as a concentrated discharge of groundwater that appears at the surface as a current of flowing water. Technically Todd (1980) describes “the thermal springs, which discharge water that has a temperature above that of the normal groundwater”. In thermal spring, the water forced up from moderate or great depths by other forces than hydraulic pressure, they may geyser and volcanic activities. The temperature of natural waters under consideration does not exceed 35°C. The temperature of thermal springs in lavas of tertiary, quaternary and recent ages was usually attributed to volcanism (Tolman, 1937).

2.1.1. Hot springs of India

Recent reports shows that, there are more than 250 springs, their groups are present in different geological setups. There is no recent volcanic activity in India except on the Barren Island of the Andaman-Nicobar islands. However, boiling with steam separation and mild geyser activity occurs at few hot springs areas in the Himalayan tectonic belt, West Coast and other parts of India. Large numbers of hot springs were generally occurs in clusters on Himalayan region. In West Coast of India, the contact of dolerite dikes with basalts along with strong crustal movements has occurred in presence of ancient rifts (Chandrasekharam and Selvakumar, 1992). Few hot springs are also located along the rivers Narmada and Sone, which was a major rift zone of the Indian land mass. A group of hot springs generally known as Rajgir-Monghyr belt has unique type of water manifest from the Pre-Cambrian meta-sediments in the northeastern part of India (Radhakrishna and Naqvi, 1986). Where, the crustal

movements corresponding to the late phase of the Himalayan orogeny have taken place towards south (eg: Tatapani hot springs). Large numbers of hot springs are also widely distributed in the other Pre-Cambrian belts of the Indian shield in areas of minor fault and shear zones (Gupta *et al.*, 1975; Gupta and Sukhija, 1974).

2.1.2. Hot Spring of West-coast India

The west coast geothermal province was considered as one of the important geothermal prospects in India (Krishnaswamy, 1976). The geothermal activity was spread over several hundred kilometers along the west coast. These areas occupies large region in the Indian peninsular and approximately about twenty thermal springs were located along the West coast in two different geological setups (Radhakrishna and Vaidyanadhan, 1997). Among the twenty springs, eighteen were located in the Deccan flood basalt Province (North Konkan). In addition, the remaining two were located in south of Konkan but in Precambrian crystalline, near Puttur in Karnataka (Irde and Banduru thermal springs) (Fig 2.1).

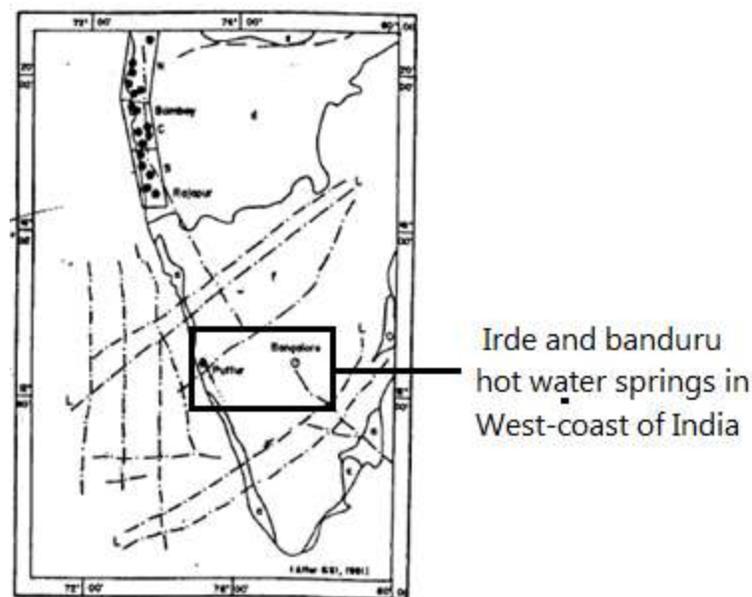


Figure 2.1: Map of hot springs location in West coast India

2.1.3. Economic importance of thermal water

The social and economic importance of thermal springs has fluctuated since civilization (Booyens, 1981; Sanner, 2000; Atkinson and Davidson, 2002; Edmunds, 2004). Over the past few decades, there has been an unprecedented interest was developed mainly due to a diversification in the application of the waters (Christopher and Armstead, 1978; Samsudin *et al.*, 1997). In addition, the increasing popularity of spas and the growing importance attached to the 'natural' health industry (Smith and Puczkò, 2009). Thermal spring waters were increasingly being used for power generation, industrial processing, agriculture, aquaculture, bottled water and the extraction of rare elements (Vimmerstedt, 1998; Lund, 2000; Baradács *et al.*, 2001; Lund and Freeston, 2001; Shevenell *et al.*, 2002; Bahati, 2003; Hellman and Ramsey, 2004; Petraccia *et al.*, 2005). In 2005, 72 countries reported on the direct utilization of geothermal energy (Lund *et al.*, 2005). A relatively recent development is the identification and use of thermophilic bacteria for possible industrial purposes (Zvauya and Zvidzai, 1995; Mawadza and Zvauya, 1996; Mawadza *et al.*, 2000; Haring *et al.*, 2005; Narayan *et al.*, 2008).

2.2. Materials and Methods

2.2.1. Study area

In Karnataka, two hot water springs have been reported from Dakshina Kannada district. Irde in Puttur and Bandaru in Belthangadi taluk. The study area for present investigation is located in Irde village in the proximity of Bettamapdi village on the Puttur to Panaje road. The thermal spring is close proximate to the Baddanthadka (also known as Seere) river (Figure 2.2). The Irde spring (Figure 2.3 a & b) is locally known as "Bendru Tirtha" bendru, bendir, or bend'r (Tulu language: boiled water). A pool has

been constructed around the hot spring and flow of water from the spring is quite weak and often dries up in the summer because of lowering of the groundwater table. Air bubbles releasing from the outlet of the spring can be noticed within the pool. The discharge temperature of the spring range from 38°C to 57°C and their waters were mainly categorized as Na-HCO₃ major ion facies like other thermal springs of west coastal India (Ramanathan and Chandrasekharan, 1997).

2.2.2. Sampling method

Due to only the partial chemical analysis was conducted before on this spring, more samples were harvested in December 2008. Two sets of water samples were collected from the thermal springs. One was from the bore well stream of the depth of 30 m and the other was the open dug well in sterile plastic container. The temperature and the pH value were recorded immediately after sampling. Thermal water samples were stored at laboratory at mild cold atmosphere until further use. Samples from bore well stream were selected for chemical analysis by employing atomic absorption spectroscopy (AAS) and titration method.

2.2.3. Determination of pH

The pH of the thermal water sample was determined in 50 ml of the water sample in a clean 100 ml beaker and using a digital pH meter (Sigma Instruments, New Delhi, India).

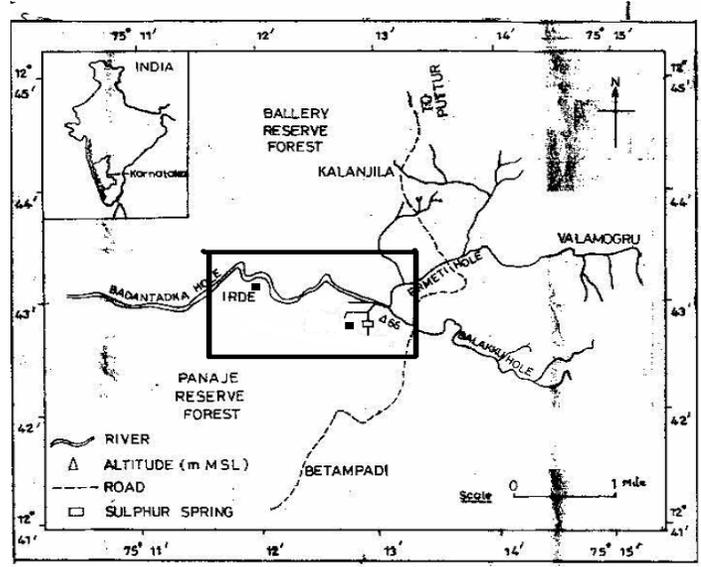


Figure 2.2: Geological map of Irde natural hot water spring in Dakshin kannada district, Karnataka.



(a)

(b)

Figure 2.3: (a) Natural hot water spring (b) Bore well hot water spring located at Irde.

2.2.4. Total Dissolved Solids (TDS) of thermal water

The TDS of thermal water was determined by measuring the weight balance of glass disc (APHA, 1977). The procedure was developed by taking the heat cleaned dish for one hour in hot air oven. Later the disc was kept in desiccators and weighed immediately before use. The samples were prepared by stirring and pipetted a measured volume onto a glass fiber filter. The glass filter was washed with three successive times with 10 ml volumes of reagent grade water. This was allowed to complete drainage between washings and continue suction for about three min after filtration. The filtrate was collected from the weighed dish and dried for at least one hr in the oven at 180°C. This cycle was repeated until a constant weight was obtained. The TDS of the thermal water sample was measured by following formula.

$$\text{TDS (mg /lit)} = (\text{A-B}) \times 1000 / \text{Sample volume (ml)}$$

Where, A = weight of dried residue + dish and B = weight of empty dish

2.2.5. Chemical analysis

Thermal water from the bore well was first divided in two sets A and B. for sample A was analyzed for elements such as Mg, Mn, Co, Cu, Fe, and other trace elements such as Ni, Hg, Ti, Sn etc., by atomic absorption spectrometer (thermo scientific, USA). Sample B was analyzed for SO₄ and HCO₃ by EDTA titration and acidimetric titration (Richards, 1954; APHA, 1977).

2.2.6. Atomic Absorption Spectroscopy (Flame AAS) for sample A

Approximately about hundred milliliter of thermal water was first acidified with 5 ml of concentrated HNO₃ near boiling. The sample was evaporated until the volume become 20 ml. Again, the sample was acidified with 5 ml of concentrated HNO₃. The

beaker containing acidified sample was covered with cover glass and boiled until complete evaporation of sample. The cover glass was washed with twenty milliliter of deionized water and filtered using Whatman filter paper 42. This procedure was repeated three to four time. All samples were collected, made up to 100 ml, and directly applied to Atomic Absorption Spectroscopy against the standard elements.

2.2.7. Determination of Bicarbonate

The estimation was based on simple acidimetric titration using different indicators that work in the alkaline (higher than 8.2) or acidic pH range (lower than 6.0) (Richards, 1954). Approximately 5 ml of the water sample was diluted with distilled water to about 25 ml and it was titrated with 0.01M sulphuric acid. Two to three drops of phenolphthalein was added to the sample before titration and shaken well. A pink color was produced indicates the presence of carbonate, and it was titrated with 0.01M sulphuric acid until the color just disappears. At this stage, alkali carbonates were converted to bicarbonate. This is called the half-neutralization stage. To this colorless solution, one to two drops of methyl orange indicator was added and continued titration with brisk stirring against 0.01M sulphuric acid (Richards, 1954; APHA, 1977). The volume consumed at all stage was recorded and calculated using the following formulae.

$$\text{Carbonates (me/litre)} = 2 (\text{Volume of H}_2\text{SO}_4) \times \text{Molarity of H}_2\text{SO}_4 \times \frac{1000}{\text{ml of aliquot}}$$

The volume of acid used for half-neutralization of carbonate is Y. Hence, for full neutralization it has been assumed as 2Y.

$$\text{Bicarbonates (me/litre)} = (Z - 2Y) \times \text{molarity of H}_2\text{SO}_4 \times \frac{1000}{\text{ml of aliquot}}$$

Where carbonate is absent: $Z \times 2$, all the values were converted in to ppm.

2.2.8. SO₄ determination of thermal water by turbidometric method

About 5 ml of the water sample was taken in a 25 ml volumetric flask. To this 10 ml of sodium acetate-acetic acid buffer was added to maintain the pH at about 4.8. Approximately one ml of gum acacia and one gram of BaCl₂ crystals was added. The volume was made up to 25 ml with distilled water. Invert the flask several times and measure the turbidity with a spectrophotometer at 440 nm using a blue filter. A standard graph was plotted by using 2.5, 5, 7.5, 10 and 12.5 ml from stock solution and was making up to 25 ml as described above. Then developed turbidity measured along with the samples. Draw standard curve was developed by plotting sulphate concentration on the X-axis and absorbance on the Y-axis. The sulphate content of the samples was calculated using the standard curve, taking into account the dilution factor of five (5 ml made to 25 ml) and expressed as ppm (APHA, 1977).

2.2.9. Piper diagram

The diagram was constructed based on the concentration of data are plotted in ppm for the cations Ca, Mg, Na, and for the anions Cl, SO₄, HCO₃ in each analysis. (Piper, 1944). The data along with the reference data was plotted on GW Chart software (Version 1.23).

2.3. Results

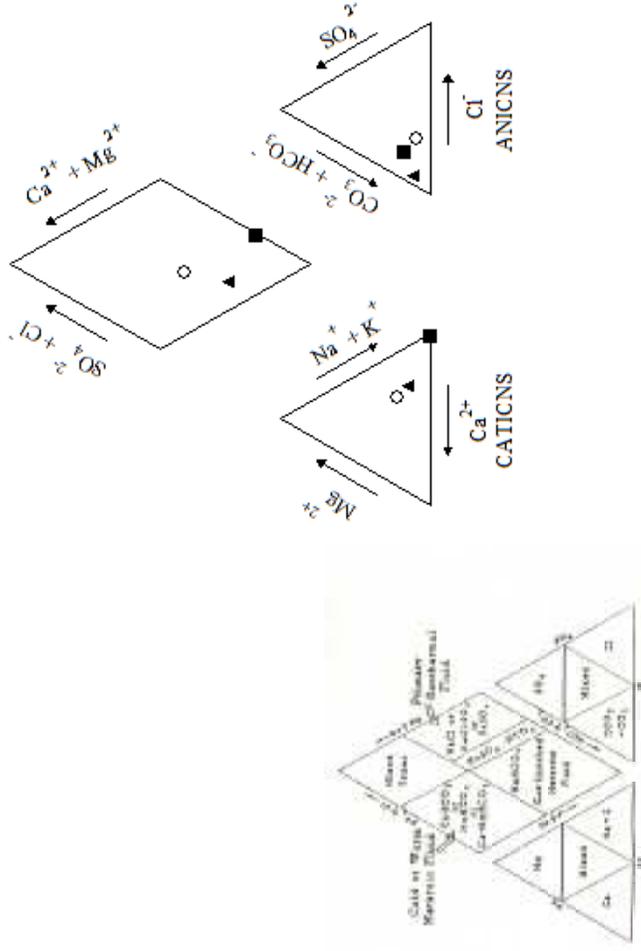
The Temperature of the thermal water was 45°C during sampling collection time (December 2008). The pH value for thermal water was observed between 8.0 and 8.4. The TDS (total dissolved solids) content of thermal waters ranges from 490 ppm to 510 ppm (Table 2.1). These parameters indicate the thermal spring was of warm temperate and slight alkaline type like other thermal springs. The analysis by the Piper trilinear

plot of Irde thermal spring indicates the same Na-HCO₃ facies like other thermal spring of Konkan region of India (Fig. 2.3).

The analytical concentration of major and trace constituents were shown in table 2.1 and 2.2. The low concentration of trace elements in the thermal water may exhibit the weak ionic interaction of the water with the rocks below the thermal spring. The great concentration of sulfur (400 ppm) was observed from the thermal water. Although, the presence of Na and HCO₃ was observed to be 209 and 301 ppm respectively. This indicates the thermal spring was previously characterized as Na-HCO₃ facies thermal springs. However, good concentration of Iron (146 ppm) and calcium (110 ppm) was observed. Other trace elements such as, Mg, Mn, Co, Cu, N, and C were present in minimum quantity ranging from (10-200) ppm (Table 2.2). The presence of Ni, Hg, Ti and Sn were not observed at detection level. This indicates that, the low concentration of trace elements in the thermal water may exhibit the weak ionic interaction of the water with the rocks below the thermal spring.

Sl no	Springs	T°C	pH	TDS (ppm)	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃
1	Irde	42- 45°C	8.0-8.4	490- 510	98	52	209	48	110	48	301
2	Banduru	37- 40°C	8.4-8.5	450-460	01	ND	114	12	32	65	163
3	Rajapur	42- 45°C	7.5-7.7	540-550	27	10	76	13	20	01	318

Table 2.1: The concentration of major chemical constituents of Irde thermal springs with reference to Banduru and Rajapur thermal springs.



(a)

(b)

Figure 2.3: (a): Standard Piper diagram (plot) of thermal water analysis. (b) Piper diagram of Irde thermal water with reference to Rajapur and Banduru thermal springs. The representations were; o-Bendruthirtha, ■-Banduru and ▲-Rajapur thermal springs. The data from this plot indicates the similarities of Na-HCO₃ ion facies like other thermal springs of West Coast of India.

Sl no	Springs	Mn	P	K	S	Cu	Fe	Sn
1	Irde	08	10	58	400	52	146	12
2	Rajpur	0.02	ND	ND	ND	ND	0.19	ND

Table 2.2: The minor chemical constituents of Irde thermal springs and comparative chemical constituents of Rajapur thermal spring.

2.4. Discussion

The Physico-chemical characterizations of Irde thermal water were shown in Table 2.1 and 2.2. The Irde thermal spring was considered as slight alkaline type like other thermal spring of West Coast and Konkan region of India (Table 2.1). Where, the observed temperature and pH was similar to that of Rajpur and Banduru thermal spring (Ramanathan and Chandrasekharan, 1997). From the previous observation, there was slight rise in the temperature from 39°C to 45°C was noted in the thermal spring due to rock water interaction was slightly higher in below the surface of the thermal spring (Ramanathan and Chandrasekharan, 1997). The pH of the thermal water was shown to be varied in 8.0 to 8.4, which was similar to the pH of other thermal spring of Konkan region area of Maharashtra (Ramanathan and Chandrasekharan, 1997). The total dissolved solid (TDS) was observed between 490 ppm to 510 ppm. However, TDS of Rajpur and Banduru thermal spring was shown to be 540 and 450 ppm respectively (Pital *et al.*, 1987).

The existing literature dealt with the Konkan region (Irde and Rajpur) thermal springs of Karnataka and Maharashtra states (Radhakrishna, 1971; Seshadri, 1974; Krishnaswamy, 1976; Pitale *et al.*, 1987). The occurrence of Banduru thermal spring was reported only recently (Selvakumar, 1991). No detailed work has been carried out on Puttur thermal springs except only partial chemical analysis of the thermal water (Ramanathan and Chandrasekharan, 1997). The thermal spring of Puttur (Irde) was of low temperature and low flow type. It falls in Na-HCO₃ facies type like Rajpur and Banduru thermal springs. The imprints of basalt thermal water interaction at Rajapur and local equilibration of doleritic dyke with the thermal water of Irde were deduced.

The reservoir of the Puttur thermal spring was likely to be located in the Precambrian formations and hence the chemical processes were similar to Rajpur thermal spring. The highest recorded sulfur concentration (400 ppm) was observed in Irde thermal spring, which was higher than Rajpur and Banduru thermal springs (Ramanathan and Chandrasekharan, 1997). Although, the calcium (98 ppm) concentration was recorded highest in Irde when compared to all other thermal springs of Konkan region analyzed previously (Pitale *et al.*, 1987).

Based on Na-HCO₃ facies characterization, the Irde was determined to have a concentration of Na (209 ppm) and HCO₃ (301 ppm). Where, the HCO₃ concentration of Irde thermal water was lesser than Rajapur thermal spring (318 ppm) and higher than Banduru thermal spring (168 ppm) (Table 2.1). Moreover, the Na-HCO₃ facies of this water implies that, the underlying reservoir of puttur (Irde) could have been located in the Precambrian rocks of the Deccan traps. It was also determined that thickness of the Deccan traps in this area was lesser than that of the North Konkan and it was concordant to the lithology (granite to granodiorite) composition of the area (Ramanathan and Chandrasekharan, 1997; Pitale *et al.*, 1987; Radhakrishna, 1971). The study on stable mineral phase was observed previously in Irde thermal water. Further studies on chemical indices of Potassium (146 ppm), calcium (110 ppm) and SO₄ was observed to be higher than Rajapur and Banduru thermal spring (Ramanathan and Chandrasekharan, 1997). This was observed from other thermal springs of the Konkan are mainly exclude Na-Ca-Cl type fluids from the reservoirs (Ramanathan and Chandrasekharan, 1997). Insight in to this, there was unavailability of literature for this highest concentration of stable phase mineral system of Irde thermal water.

On the other hand, there was only partial chemical analysis was conducted previously; further work was extended to determine the trace elemental composition of Irde thermal water. The trace elements such as, Magnesium, Manganese, Cobalt, Copper, Nitrate, and Carbon were present in minimum quantity ranging from (10-200) ppm. However, there was no detailed work has been carried out on Rajapur and Banduru thermal spring. The presence of Ni, Hg, Ti and Sn were not observed at detection level. This indicates that, the presence of low concentration of trace elements in the thermal water could exhibit the weak ionic interaction of the water with the rocks below the thermal spring.

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