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Problems of Scaling and Corrosion in Geothermal Water: Indian Scenario

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***Abstract*: India is looking at tapping the geothermal resources that are available at majorly seven regions in India. India is ranked low in terms of Geothermal potential with low/medium heat enthalpy but there are enough resources with temperatures in the moderate to high range to generate power through hybrid systems if not independently through geothermal. There are a few geothermal power plants in the pipeline but nothing significant on the ground as yet. Since the water from geothermal sites is not chemically inert or pure, there is always the problem of scaling and corrosion in the power plant setup. Silica scaling has long been a hurdle in efficient power extraction from geothermal resources. In relation to this problem, data from all of these seven Indian geothermal provinces was extensively analyzed to draw conclusions on the locations which are the most feasible locations for setting up power plants based on the comparison of several chemical factors such as hardness, pH and composition of water from various sites. Although this is just a suggestive feasibility based on chemical aspect of thermal fluids, yet this aspect is a vital one. Also, the scope of chemical extraction from these sites is discussed. Extracting the minerals from the geothermal fluid would not just safeguard the plant from the problem of scaling and corrosion but also reduce the cost of power generation by contributing to the profitability.**

***Keywords*: Geothermal Energy, Green energy, Corrosion, Extraction, Scaling.**

1. Introduction

Today, when countries round the globe are looking to meet the ever increasing demands of their energy for their residents, the need to shift towards newer and green renewable resources can be denied by none. If these new resources are also capable of somewhat making the population self-sufficient in meeting their energy needs, there cannot be a better blessing than this for the countries like India where the gap between energy demand and supply is widening by the hour. This is probably the biggest reason and benefit behind the success of solar energy in India because it makes a common man a little independent by generating own electricity at home. One such resource can be Geothermal which is still widely untapped on a global scale. Geothermal Energy is the renewable underground energy which is available in the form of heat. This won't provide every commoner the power to drill at his home and use geothermal water for power generation because this comes with its set of foundations as well. Common man cannot generate electricity through this but communities can manage to set up infrastructures to use the geothermal fluids to meet thermal domestic needs but only if it is geographically viable at their location. Most vital advantage of this resource over other resources is its availability all-round the year independent of the weather. It has been estimated that heat energy within the 10,000 metres of earth's surface is 50,000 times more than all the oil and gas resources worldwide [1].

The temperature, composition of fluid, pressure, mass flow rate and many other factors vary from place to place like for every other natural resource. Depending upon these factors, the utility of geothermal resource varies from direct domestic heating to power generation to mineral extraction. Low temperature fluids can be used for domestic purposes, agriculture, horticulture etc. Medium temperature range fluids of around 300K can be used for power generation while the higher temperature range fluids can be used for industrial applications as well. Geothermal fluids can also be seen as a source for extraction of some metals and minerals. Since this fluid comes in contact with various rocks and ores inside the earth's surface and that too under high pressure and temperature conditions, the fluid is bound to pick up minerals and metals in some or the other form from there. This leads to the unavoidable menace of scaling and corrosion of all the pipelines and tanks that the geothermal fluid comes in contact with. One of the principle conditions of extraction is the economical side of it, the process and the end result that is the extracted mineral should be economical to extract from this water. This would require a balance between low concentration of the mineral and high cost of extracting it. Only when both of these factors are worked out to provide a profitable layout can the extraction be done. With time, the cost of power generation through geothermal sources is also coming down and becoming more and more competitive. This also makes this resource a promising as well as a fulfilling one.

2. Review of literature

Cinti et al. in their paper discuss about the geochemistry of several areas in India and they concluded that the surface temperatures in Himalayan region are generally on the higher side, it being higher in the Parvati Valley than the Beas Valley. While circulating at depths inside earth's surface, the water picks up saline nature due to its interaction with rocks. The relatively high salinity of Sohna spring points to longer residence time or circulation in crust. Dissolved hydrogen in huge amounts was also found in roughly all the samples assessed from Parvati, Beas and Sohna region which pointed towards fault activity [2].

Corrosion rates were assessed by Cabrini et al for various chemical compositions over a period of 7 months of exposure. Initial exposure led to the formation of layer of corrosion products for a brief period at a high rate which tends to decrease for subsequent exposure. The layer acted as protective inert layer for a short period before flow condition overcome it to increase the corrosion rate again. As the scales thicken their adhesive properties decreases and hence the rate of corrosion increases rapidly in the longer run [3].

Discussing about the scaling problem in Geothermal heat systems, K. Rafferty talks about water chemistry and how scaling is often overlooked in the GHP operation. For the open loop usage of heat pump, scaling can be a common problem as the water is directly used repeatedly. But in the case of closed loop, concern shifts towards the desuperheater. Hardness and alkalinity can give clear indications about the chance of scaling. Most common form of scale is that of Calcium Carbonate which can be attributed to the groundwater that is used. Carbonate Hardness that includes the carbonates and bicarbonates of Calcium and Magnesium then there is non-carbonate hardness which can be characterized by comparatively greater solubility. It is the Carbonated Hardness that is a major scaling promoter. Alkalinity is a measure of how able the water is in neutralizing the acid. Water quality problems also increase with the subsequent increase in Total Dissolved Solids (TDS). Two commonly used indices in the water treatment applications are Ryznar Stability Index (RSI) and Langelier Saturation Index (LSI). Since both these indices are based on the saturation point of carbonates, they provide a better image of scaling than corrosion. Lime deposition increases with the increase in water usage and it also increases with the increase in temperature of the water. Scale formation as indicated by LSI, increases with increase in pH and is evident beyond a pH of 7.5. A scale formation of .03 inches on heat exchanger system can increase the power consumed by 19% at the operation conditions of 55°F in GHP. To qualitatively determine the degree of scaling, we need the information of several factors such as TDS, pH, calcium hardness, and temperature. pH determination should be treated as primary indicator and if it is found to be greater than 8, relevant data should be gathered to determine RSI and LSI. Weak acid can be circulated through heat pump to remove the scale periodically [4].

Pierre Ungemach discusses the solutions to this problem of scaling and how it can be handled better for low enthalpy Geothermal Environments. Damage diagnosis is the first step in recognizing the problem and then addressing it. It can be diagnosed in several ways. One such diagnosis is through the assessment of pressure and flow characteristics. Others are direct damage assessment through inspection by ultrasonic, production tools and multifinger calipers. The scale removal is conventionally achieved by cleaning the well through rockbits which are drill driven or hydrojetting tools. Weak acids can also prove to be an efficient damage remedy for this scaling problem when dilute acid is periodically injected into the system. The chemical inhibitors can also be used to mainly address two concerns that is to prevent corrosion and attack scales. Sulphate reducing bacteria promotes microbiological corrosion which is a serious cause of damage to injector wells in particular.[5]

3. Chemistry of geothermal fluids

Geothermal fluids constitutes of a wide variety of dissolved chemical species in different concentrations. Geothermal fluids can be characterized by frequently cited parameters such as TDS (Total Dissolved Solids) and pH of the fluid. TDS or Total Dissolved Solid is measured in parts per million (ppm) or milligram per litre (mg/L) and it gives the estimation of the amount of chemical salts dissolved in the geothermal fluid. The TDS value of geothermal fluid varies from few hundred to more than 3,00,000mg/L, whereas in high-temperature geothermal regions the TDS lies between 6,000 to 10,000 mg/L. In geothermal fluids, the nature and quantity of dissolved chemical salts and species depend upon the local earth's structure or geology and the temperature of geothermal fluid. Generally, it is noted that the amount of dissolved solids in low-temperature resources is lower than that of dissolve solids in high-temperature geothermal resources. Another parameter pH denotes acidity or basicity of the geothermal fluid. The acidic or corrosive fluids have a pH of less than 7, and the alkaline fluids have a pH of greater than 7. In the case of neutral fluids, their pH should exactly be equal to 7 at room temperature. Mainly the pH of geothermal resources lies between moderately acidic (5.5) and moderately alkaline (8.5) [6]. In low temperature geothermal water the dissolved solids majorly composed of silica (SiO_2), calcium (Ca), sodium (Na), potassium (K), chlorine (Cl), sulphate (SO_4), and bicarbonate (HCO_3). The geothermal fluid also contains various elements such as mercury (Hg), fluorine (F), boron (B), and arsenic (As) in small amounts [7]. Arsenic, being toxic if present in higher concentrations is of environmental concern and it has to be eliminated before extraction of other materials. In geothermal resources the gases are also dissolved in the fluids. Majorly dissolved gases include ammonia (NH_3), carbon dioxide (CO_2), hydrogen sulphide (H_2S), and methane (CH_4) [7]. Hydrogen sulphide dissolved in geothermal fluids is toxic and dangerous for animals as well as humans. As the geothermal fluid flow it interacts with surrounding rocks and reacts chemically to form chemical compounds or minerals. Carbonates, sulphates, and silica are produced as a result of these complex chemical reactions. Some of the minerals either dissolved fully or some of them are precipitated from solution and in some cases even substitution of elements within a mineral takes place. These changes may or may not attribute to volume changes of the reservoir rocks, which means the porosity and the permeability of the rock may or may not be affected due to these chemical reactions [6]. If we consider the case of silica and calcite, the solubility of silica in geothermal fluid decreases with decrease in temperature of fluid whereas the pressure change has negligible effect on solubility of silica. So, SiO_2 generally precipitates due to abrupt change in temperature of subsurface, in pores or fracture in the rocks. But the case of other minerals like calcite (calcium carbonate, $CaCO_3$), dolomite (magnesium carbonate, $MgCO_3$), and sulphate species is totally opposite i.e. these minerals have higher solubility at lower temperatures than at high temperature [6].

In above paragraph, we came to know about different chemical compounds and gases which are dissolved in geothermal fluid. Upon exploitation the fluid undergoes thermodynamic changes which results in scaling, corrosion of surface in contact with fluid and sometimes environmental problems of liquid disposal and emission of toxic gases like H_2S [8]. Scaling can be described as a process of accrual or collection of undesirable material on the surfaces which interact with the geothermal fluid. The scaling is common phenomenon and can be observed in geothermal power plants and also in reservoir surroundings. It is a very rapid, rampant, and complex process. It depends upon various factors such as pressure and temperature of geothermal fluid, operating conditions and time of interaction between fluid and rock. When the geothermal fluid boils, dissolved gases are released due to which pH level of fluid increases and it becomes more alkaline due to which metal sulphides and calcites are formed. These minerals form hard scales on inner portions of surface pipes and well casing [9]. Normally crystallization scaling takes place in geothermal installations when the ionic product of less soluble salt becomes greater than its equilibrium solubility product [8]. Common forms of scale include carbonate minerals ($CaCO_3$), metal oxides, amorphous silicates (SiO_2), and sulphides. The most profound geothermal scales are of calcite ($CaCO_3$), and silica (SiO_2). The colour of both these scales is white and these cannot be distinguished by naked eyes. Sometimes due to corrosion in geothermal fluid pipe, iron sulphide is formed due to which the silica scales tends to appear grey or black [10]. To estimate the scaling potential of the geothermal fluid its TDS, pH, temperature, total hardness, and total alkalinity should be known. Usually the scaling problems are common for fluids whose pH value is above 7.5 [6]. Various methods are available to prevent and control scaling in geothermal systems. The most used methods include adding of scaling inhibitors, acidifying geothermal fluid to maintain mineral equilibrium, proper construction of geothermal plant, and by removing scales chemically or mechanically [8].

Another harmful effect of geothermal fluid is corrosion of systems used for handling fluid and also of the equipment used for utilization and exploitation of geothermal fluid [8]. The effects of corrosion of geothermal fluid are influenced by the chemical composition of fluid. The qualitative features of geothermal fluid such as lower pH, high concentration of salts and dissolved gases increase the corrosion potential. The geothermal fluid contains a wide variety of dissolved components varying from halogen acids to strongly sulphur containing acidic fluids to neutral or alkaline pH water, which effectively corrode most of alloys and even remove the protective layer formed due to scaling of silica, calcite or metal oxide. The chemicals species which are present majorly and make geothermal fluid highly corrosive are chlorides (Cl^-), sulphides (HS^-), sulphate (SO_4^{2-}) and bicarbonates (HCO_3^-). Further presence of oxygen, hydrogen ions, and fluorides supplements the corrosion of metals [8]. The rate of corrosion is enhanced if geothermal fluid is contaminated with oxygen. Other factor which affects rate of corrosion is release of dissolved gases because it is seen that as the dissolved carbon dioxide are released, the pH of geothermal fluid tends to increase. The rise in pH of fluid reduces the effectiveness corrosion action on steel. The flow conditions of geothermal water like turbulent flow and stagnant water conditions also increase the corrosion potential [6]. The different types of corrosions that are evident in geothermal installations are uniform corrosion, pitting, crevice, sulphide stress cracking, stress corrosion cracking, under deposit corrosion, galvanic corrosion and impingement. Components which are more sensitive towards corrosion are steel casings, screens and heat exchangers. In order to prevent corrosion the first step can be use of noble metals if there are no economic or technical constraints. Corrosion can also be limited by using corrosion resistant materials such as plastics or by not coagulating materials with distinguished electro-chemical potential. Coated pipes and casing can also prevent the problem of corrosion. Coating can be done by using thin plastic or epoxy layer on inner surface of pipes [6].

Some of the dissolved chemical components of geothermal fluid have a value and can be utilized if they can be easily extracted, separated, and purified. The valuable minerals can be recovered from geothermal resources, whether they are present in solid geothermal residues like scales and sludges or in the geothermal fluid. The process of extraction should be economical, profitable, and technically feasible, and the mineral should be available in abundance in the geothermal resource. The main chemical compounds extracted are silica, lithium, and alkali metals. The other subsidiary products that can be recovered are some inexpensive salts like NaCl, $CaCl_2$, and some other salts. Minerals like limestone and metals like gold and silver can also be extracted inexpensively [6]. The process used for the recovery of minerals from solid materials like sludges and scales is acid leaching and biochemical leaching. Acid leaching is generally used for extracting silica in pure form, and in this process hydrochloric acid is used to leach iron from the residues. Biochemical leaching is the process utilized for the recovery of metals from low-grade chalcopyrite and aurum ores. The process is carried out in the presence of acid-loving bacteria which leach out toxic metals. Sometimes

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the residual products in this process are refined such that they can be used directly for further applications. Sorption, Evaporation, Precipitation as sulphides can be used to recover metals from geothermal water. Uranium, cobalt, zinc, manganese, and lithium ions are recovered by using synthetic resins, which adsorbs ions from the solution in the sorption process. Silica is very harmful to a geothermal resource as it causes scaling due to which geothermal resources cannot be utilized properly. In order to extract other minerals silica should be removed firstly. Silica can be removed in the form of quartz (SiO_2). Most of the geothermal resources have lithium in abundance, so these resources become a rich source of lithium extraction. By precipitation of lithium salts directly in the fluid lithium can be extracted. The main problem which arises during the extraction process is that despite the high concentration of precious metals in the resources it may not be convenient to extract these metals purely as the process involved will be complex, expensive, and risky.

4. Geothermal resources of India

Organized synergic research, development and corroboration program is being ventured by several organizations such as Geological Survey of India, National Aeronautic Limited, Bangalore, IIT Delhi, National Geophysical Research Institute (NGRI), ONGC, etc. As per the research analysis from different case studies and audits, locations of 350 inherent hot springs, scattered in around seven provinces have been determined all over the country. A persistent surface temperature range from 37°C - 90°C with an increasing surface discharge of 1000 l/m has been identified. Out of the water resources that have been identified a maximum number of them are of low temperature, which would be used in thermal applications. Only a certain number of locations are being identified where a spawning 10,000 MW of electrical power has been predicted. Small prototype plants have been made to utilize the geothermal resources to accumulate power from the resources present at Puga and Chumathang (Ladakh, J&K) and Manikaran (HP). The provinces are being divided as per their locations as The Himalayas, Cambay, Godavari, Sohana, Mahanadi, West coast, and Son-Narmada-Tapi (SONATA). The above provinces are affiliated with fissures or diminution tectonics where the flow of heat and the gradient of geothermal energy is optimum.

In some particular locations such as Puga valley of Ladakh and J&K and Tattapani (District Sarguja), Chattisgarh, these intermediate enthalpy geothermal reservoirs have been relevant in power generation with the help of a Binary Cycle structure. After an extensive research, a hydrothermal reservoir at a depth of 3 km at 260°C temperature in Tattapani has been determined by NGRI, Hyderabad.

To tap the inherent geothermal energy, the Ministry of New and Renewable Energy Resources have planned to develop the Puga valley in Ladakh (in March 2008 by Union Ministry of New and Renewable Energy). An estimated cost of the installation of the 300 kW electric power plant was around Rs 4.6 crore. Extensive research of Badrinath-Tapovan in Uttaranchal, Satluj-Spiti, Beas and Parbati valley in Himachal Pradesh and Surajkund in Jharkhand have been undertaken by NGRI, Hyderabad to get an optimized location to generate a Renewable source of Power and could cover only diminutive industries as most of these resources are situated in rural areas.

Fig. 1. Location of the seven geothermal provinces in India (Source: indiaenergyportal.org)

In The Himalayan province, the main location is Puga valley (J&K), and Manikaran (HP) with a heat flow rate of 468 mW/m^2 and a thermal Gradient of 234 °C/km, a thermal gradient of 76-96 °C/km in Sohana province has been determined. The Main location in West coast province is Unai (Maharashtra) with a heat flow of 129 mW/m^2 and a thermal gradient of 59 °C/km. Tuwa (Gujarat) is identified as the main location in Cambay province with a heat flow rate of 93 mW/m2 and a thermal gradient of 70°C/km. The Son-Narmada-Tapi province is present on the Deccan Plateau with main locations as Jalgaon (Maharashtra), Tattapani (Chattisgarh), Bakreshwar (Bihar) with a heat flow rate of 120-260 mW/m^2 and a thermal gradient of 60-90°C/km. The heat flow rate of 104 mW/m^2 and thermal gradient of 60°C/km has been determined in the Godavari province in the last province Mahanadi a heat flow rate of 200 mW/m^2 and a thermal gradient of 90°C/km has been determined. All this extensive data research has been done by the National Geophysical Research Institute (NGRI), Hyderabad along with the Ministry of New and Renewable Energy.

5. Analysis of the seven geothermal provinces of India

Data from over 500 geothermal sites across the seven Indian provinces was collected for analysis from the official site of Ministry of New and Renewable Energy, Govt. of India. Geothermal Atlas of India [11] and Geothermal Resources of India[12] document the data from the geothermal hotspots spanning all over the country. It contains data for the chemical composition and concentration of various ions for every site. TDS, Silica concentration, Temperature and pH which form the basis of primary indication of scaling, were studied and general trends governing their interdependencies were found out. Data was segregated into Himalayan Province and other six provinces were clubbed into non-Himalayan provinces for better analysis and comparison. Himalayan Province was found to be roughly on the higher side on all of these parameters in comparison to other non-Himalayan provinces. Himalayan province includes all the regions lying along the Great Himalayan belt including the areas Jammu and Kashmir, Uttarakhand, Himachal Pradesh and Northeastern hilly areas.

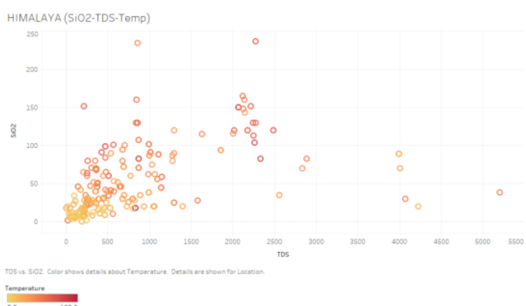

Fig. 2. Concentration of SiO_2 vs. TDS curve with temperature as color gradient from sites of Himalayan Province

As the plot for Himalayan Province sites between concentration of SiO_2 and TDS (Fig. 2.) shows there are more dots on the red side of the temperature scale which indicates how temperature close and above 100°C are common in the region which can be used for the heating purposes as well power generation. Sites like Tapovan, Yurdu, Jamnotri and Manikaran were found to have temperatures on the higher side with comparatively lesser concentration of TDS and SiO_2 which makes them ideal for plant setup for power generation. Tapoban is already under the lens for the scope of power plant setup by the government agencies. On the other hand sites from Puga Valley, Ladakh were found to have the temperatures on the higher side of spectrum but with also a significant presence of Silica and TDS. This means this site will be prone to scaling and would require regular chemical treatment or silica extraction. Puga Valley is an important site for Geothermal in India which has been the centre of focus and poses high potential for meeting the targets of Ministry of New and Renewable Energy (MNRE) of power generation through Geothermal.

The plot between TDS and Temperature from the sites of Himalayan Province (Fig. 3) shows more and more dots with blue color which means more sites have pH more than 7.5 which is when the scaling occurs. Going by just the pH cut off mark, it makes most of the Himalayan sites prone to scaling. The general trend from the data of the sites also suggests how TDS increases gradually and exponentially with the increase in temperature.

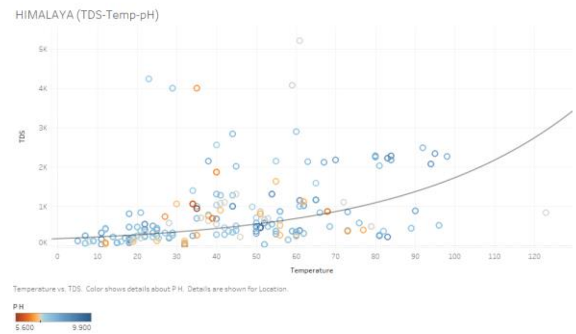

Fig. 3. TDS vs Temperature curve with pH as color gradient from sites of Himalayan Province

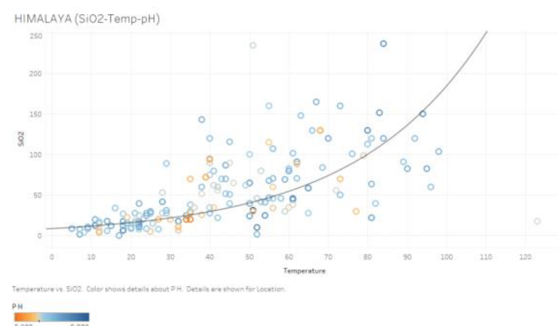

Fig. 4. Concentration of SiO_2 vs. Temperature curve with pH depicted as color gradient from sites of Himalayan Province

The plot between concentration of SiO_2 and Temperature (Fig. 4) also suggests that there is exponential increase in the concentration of Silica as the temperature of the water increases. This indicates that the sites which will be targeted for power generation with higher temperatures will be prone to siliceous scaling and have concentrations in extractable ranges for Silica.

The plot between the concentration of SiO_2 and TDS for the six non Himalayan provinces (Fig. 5) is found to be scattered one but a major cluster for almost all the six provinces is found to be located on lower TDS and lower silica concentration sides are found. This points to lower scaling and corrosion problem in these areas. This can also be attributed to the moderate temperatures of geothermal water in these locations. These moderate temperature ranges are useful for domestic purposes and industries where high temperatures are not needed. Since scaling tendencies are low in these regions overall, there won't be any need for extra care and expenditure to prevent the same.

The plot of TDS and Temperature curve for the six non Himalayan provinces (Fig. 6) depicts the general trend of exponentially increasing TDS with increase in temperature for four out of the six provinces. It comes out to be gradually and slightly increasing for Godavari Province and almost a constant trend for Mahanadi Province. Mahanadi remains a low TDS zone for all the temperature ranges and all the geothermal sites.

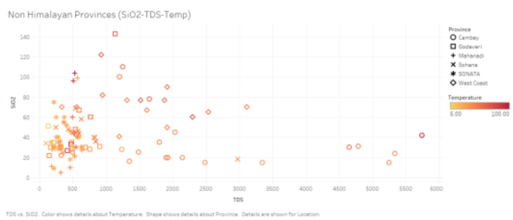

Fig. 5. Concentration of SiO_2 vs. TDS curve with Temperature as color gradient from sites of all six non Himalayan Provinces

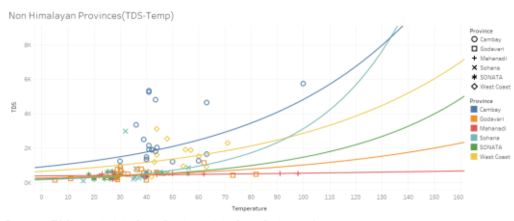

Fig. 6. TDS vs. Temperature curve from sites of all six non himalayan provinces

Tattapani sites also rank high on the temperature scale which makes them the best prospect for power generation as well as industrial heating usage. There is manageable risk of scaling with sufficiently high temperature. This also goes in line with the government's efforts to harness Tattapani geothermal resource alongside Puga Valleya and Tapoban sites in the Himalayan region.

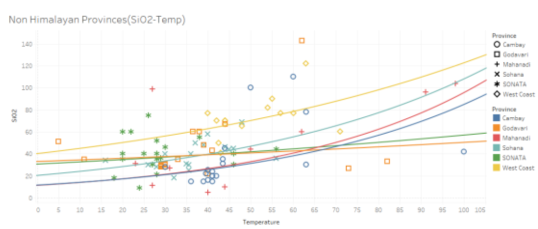

Fig. 7. Concentration of SiO_2 vs. Temperature curve from sites of all six non Himalayan provinces

The plot between concentration of SiO_2 vs. Temperature (Fig. 7) does not reveal any general trend for these six provinces. However, it appears to be scattered with some clusters of individual provinces in the middle which can be due to the compact and small areas of these provinces. Due to this there is some scope of uniformity in the temperature ranges and chemical composition. The trend lines depict increasing tendency of the silica concentration with the temperature.

6. Conclusion

Study and analysis of the data of indicators for scaling and corrosion such as pH, Temperature, concentrations of SiO_2 and TDS was carried out. It was observed that the Himalayan provinces appeared to have higher temperatures in general than the non-Himalayan provinces sites. There is exponential increase in TDS and silica concentration with increase in Temperature. Puga Valley in Ladakh, Tattapani in Chhattisgarh and Tapoban in Uttarakhand were found to be ideal sites for plant setup in line with the government agencies' efforts in tapping geothermal resources at these sites. Mahanadi, Godavari, SONATA provinces were found to have lower TDS values in general which make them viable sites for domestic and moderate industrial usage without high hazards of scaling and corrosion.

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