



UNITED NATIONS
UNIVERSITY

UNU-GTP

Geothermal Training Programme



SAMPLING AND ANALYSIS OF THE FLUIDS COLLECTED FROM TWO-PHASE WELLS

Iwona Galeczka

Iceland Geosurvey (ÍSOR)
Grensásvegur 9, 108 Reykjavík
ICELAND
iwona.m.galeczka@isor.is

ABSTRACT

The standard operation procedures for sampling and analysis of two-phase wells used during the well discharge test and during the regular production stage are very similar. A portable Weber-type separator is attached to the well head allowing to collect liquid and steam phase separately. The analytical results of both phases (so called discharge data) are recalculated to the chemical composition of the deep fluid using geochemical computer codes with appropriate thermodynamic database. Proper sampling and analysis of well fluids is the first step in long term process of understanding the system and predicting its response to the production. Therefore, care has to be taken when choosing sampling container types (glass or plastic, amber or transparent), pre-treatment and preservation methods (dilution, filtering, addition of chemicals), and analytical techniques. These have to be adjusted to the physicochemical conditions of the sampled fluids since the interpretation of the results is confined by the quality of the data.

1. INTRODUCTION

Geochemical methods are used at all stages of geothermal utilization namely exploration, development and production. At all these stages, it is necessary to collect fluid samples which later can be analyzed and obtained results can be used for interpretation of the physicochemical conditions within the deep aquifer of interest. Results and interpretation of fluid sample composition contribute to the development and improvement of reservoir conceptual model. In addition, experience show that frequent sampling and continuous monitoring are often the only way to notice deep fluid chemical changes caused by the exploitation activities e.g. injection within the geothermal system (e.g. Galeczka and Óskarsson, 2019). These changes are done regularly, and monitoring should be minimum in the same frequency as production variables are changed in order to observe changes caused by these variations. However, these changes are not seen immediately. There is a need of at least several observations for chemical trends to be noticed and to link them with the activity that was performed in the past. If the sampling frequency is low, changes might never be observed. Recognition of the chemical changes in time improves our understanding of the geothermal system and gives better chance to predict the response of the system to the production intensity in the future.

This short report summarizes the standard operation procedure used for two-phase well sampling (Figure 1). It also contains guidelines for interpretation of the chemical data obtained from samples collected during the well discharge test. In addition, it presents a general overview of the Tracer Test Flow (TFT) measurements for assessing the production well mass flow and discharge enthalpy. Its content is based

on number of publications (including Iceland Geosurvey ÍSOR internal reports) in which detailed descriptions of these procedures have been presented. To complement information given here, the reader is referred to the publications listed in references section (e.g. Arnórrsson, 2000; Arnórrsson et al., 2006; Axelsson, 2018; Ármannsson and Ólafsson, 2006; Óskarsson and Ármannsson, 2017; Thorbjörnsson et al., 2013; Lovelock, 2001).

2. SAMPLING AND ANALYSIS OF TWO-PHASE FLUID

2.1 Safety during sampling

First and foremost, handling of geothermal fluids which are hot, pressurized, corrosive and contains toxic gases (H_2S) pose a life threat to a sampling personnel. Therefore, ensuring good ventilation, protective clothing and equipment for ears and eyes and fast access to the safety relief kit is crucial. A personal gas detector has be worn during sampling and working place should be abandoned if the H_2S concentration in air exceeds 10 ppm(v). In addition, some of the reagents used for sample preservation are corrosive (e.g. NaOH and HNO_3) and therefore they should be handled carefully. All the connections (hoses, valves) have to maintain the pressure and therefore their regular maintenance should be a part of sampling operation procedure. The personnel should be trained in responding to hazards possibly happening during the sampling.



FIGURE 1: Sampling of the two-phase well during the discharge test. The well head is connected to a transportable steam separator which discharges steam into the air and water into a weir box where fluid flow is quantified (e.g. Axelsson, 2018).

2.2 Sampling containers

Glass and amber containers with airtight caps should be used for collecting samples for constituents which are sensitive to atmosphere (pH, dissolved CO_2 , δH and $\delta^{18}O$ isotopes), and light NH_3 . Containers should be rinsed at least three times with the sampled fluid prior to collection. For lightness, ruggedness low density or high-density plastic bottles are used. The disadvantage of the plastic containers is its permeability which allows the liquid samples to interact with the atmosphere resulting in fluid composition changes during the storage due to evaporation, dissolved gasses diffusion, and grow of microorganisms. These processes modify the chemical composition of the fluid by changing the redox and saturation state of the fluid with respect to minerals what may result in removal of certain components by oxidation and consequently secondary phases precipitation. Plastic material characterises in high adsorption capacity and therefore it might decrease the mobility of cations in the fluids. Glass is fragile and relatively heavy but with a properly constructed cap it can be easily airtight.

2.3 Preservation of samples and analytical methods

Interaction of the water sample with suspended inorganic and organic matter, adsorption on the walls of the containers, biological activity, redox reactions, polymerization and precipitation are the most common processes affecting the chemical composition of the samples during its storage. Various preservation methods are used to account for these processes and therefore during the sampling several aliquots of the same sample is taken (Figure 2). Note that the choice of preservation methods depends on the analytical methods which will be employed later. The most common physical and chemical preservation methods are shown in Table 1 assuming that the constituents of interest will be analysed using assigned analytical techniques.

Hot liquid samples have to be immediately cooled down to an ambient temperature to avoid evaporation using a cooling device, which is usually a stainless-steel cooling coil immersed in cold water, during collection. Steam samples collected into NaOH in double-port bottles (called Giggenbach bottles) bypass the cooling device, however, the bottle itself during the steam collection has to be cooled by regular short-term immersions in the cold water.

The determination of the dissolved H₂S in a liquid phase has to be performed *in situ*. Substantial losses of H₂S due to diffusion and oxidation are observed during the storage and transportation to the laboratory. When collecting aliquot for cations, trace metals and isotopes, liquid samples have to be filtered using 0.2 µm cellulose acetate inline filter. Note that condensate samples for cations and isotopes analysis do not require filtration unless suspended matter is expected to be present in the condensate.

TABLE 1: Analytical and preservation methods used for constituents of interest present in high-temperature geothermal fluids.

Analyzed constituent	Analytical method	Preservation methods
Liquid phase		
pH, CO ₂	CO ₂ titration	Airtight amber glass bottle, determination within 48 h
NH ₃	UV-VIS ¹	Airtight amber glass bottle
SiO ₂	Spectrophotometry	
Anions (Cl, Br, SO ₄ , NO ₃)	Colorimetry	Dilution with DI water if SiO ₂ >100 ppm
Cations, trace metals	IC ²	Filtration
	ICP-OES ³ /MS ⁴	Filtration; acidification using HNO ₃ (Suprapur) acid (1% v/v). Acid washed containers for trace metals
SO ₄	IC	Filtration; addition of 0.2 M ZnAc ₂ (if H ₂ S > 1 mg/L; 2% v/v), and additional filtration to remove precipitated ZnS
H ₂ S	Titration	Analysis done <i>in situ</i> using HgAc ₂ and dithizone as color indicator
δ ² H, δ ¹⁸ O	MS	Filtration, airtight amber glass bottle
Steam phase		
Condensate		
NH ₃	Spectrophotometry	Airtight amber glass bottle
Na, B, and other cations of interest	ICP-OES	Acidification using HNO ₃ (Suprapur) acid (1% v/v).
δ ² H, δ ¹⁸ O	MS	Airtight amber glass bottle
Vapor		
Gases	GC ⁵ and titration	Added to 50 mL 40% NaOH in evacuated double port Giggenbach bottle. CO ₂ and H ₂ S are analyzed using titrations methods (as described above), the rest using GC

1: UV-VIS – Ultraviolet Visible; 2: IC – Ion Chromatography; 3: ICP-OES – Inductive Coupled Plasma – Optical Emission Spectroscopy; 4: MS – Mass Spectrometry; 5: GC – Gas Chromatography.



FIGURE 2: Sample aliquots collected during single sampling of two-phase well. Liquid (Lq.), condensate (Cond.), and vapour sample are taken into appropriate containers and preserved for further analysis according to Table 1.

2.4 Selection of sampling points

Sampling from a two-phase well head requires using a Webre-type separator (Arnórsson, 2000; Figure 3) to separate the liquid and steam phase. It has been shown (Ellis and Mahon, 1977) that the most representative samples are collected from the flow of a two-phase well at about 1.5 m distance from the T-joint at the well top. If this is impossible samples should preferably be collected 1-2 m downstream of a bend, valve, orifice plate or other constriction points in order to allow well mixed fluids to flow into the separator rather than laminarly flowing fluid that might have undergone separation due to gravity. For excess enthalpy wells characterized with high vapour fraction, samples should be collected at a pressures close to the well head pressure.

By regulating the separator outflow from sampling ports (through the outflow valves on liquid and steam ports; Figure 3) the water table inside the Webre separator is adjusted in order to obtain good separation of both phases. This is crucial for further analysis and calculations of the deep fluid composition. The quality of separation can be assessed to some extent in the field, during sampling by visual inspection of the vapour phase exiting from the separator. When collecting a steam sample, low water table and therefore dry vapour phase exiting the steam sampling ports suggests proper separation inside the separator. And it is confirmed by the absence of steam droplets (transparency) at the very close of the vapour sampling port (Figure 3, left).

On the other hand, when collecting the liquid phase, high water table in the separator should result in visible liquid carryover at the separator steam sampling outlet (Figure 3, right). The separation efficiency can also be evaluated during the sampling by measuring the conductivity of the condensate (should be very low) and the liquid (should be much higher than that of condensate). The concentration of a non-volatile such as Na in the condensate can be used for calculating the liquid fraction in the condensate.

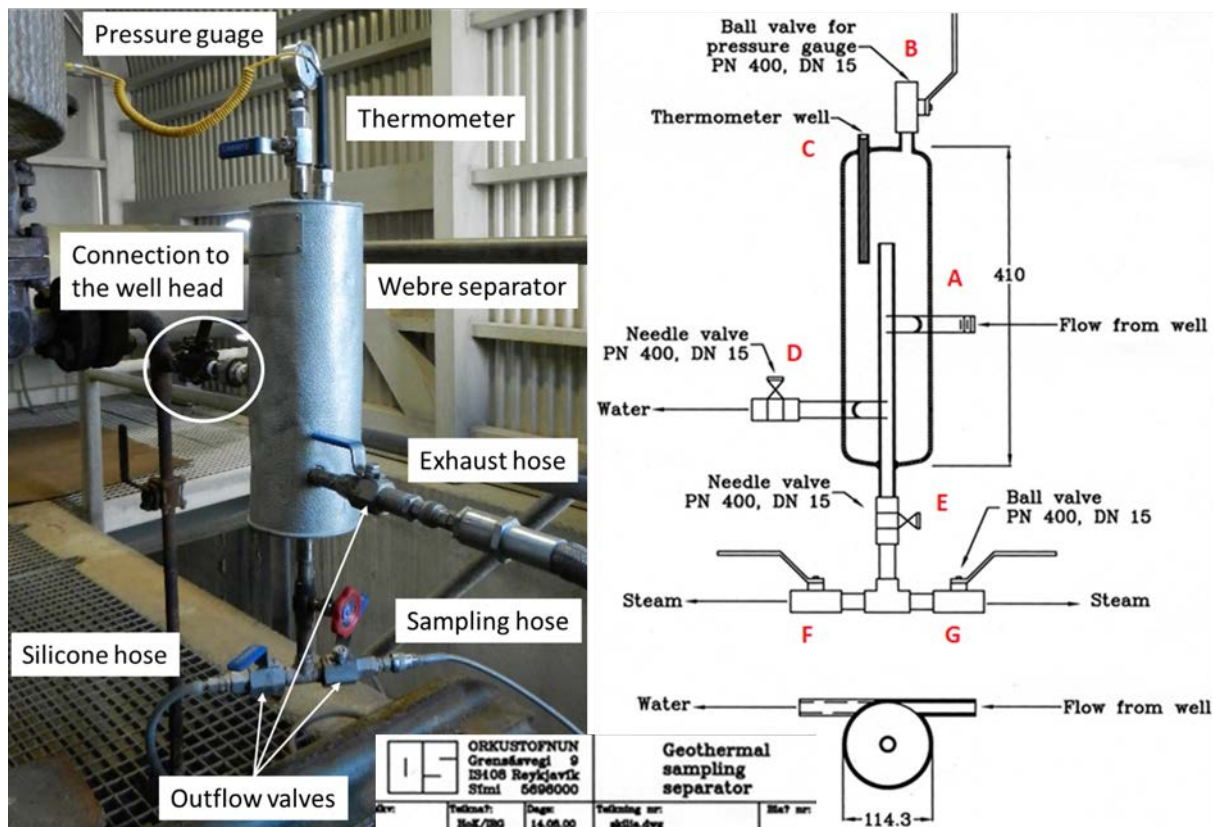


FIGURE 3: The Webre-type separator connected to the well head of the two-phase well with additional equipment needed during sampling (left). The most important parts of the separator are shown in the technical drawing (left).



FIGURE 4: Steam sampling outlet on a Webre separator releasing a dry vapor (left) and a mixture of liquid and vapor (right).

2.5 Sampling procedure using Webre-type separator

- The connection of well head or two-phase pipeline is opened for a few seconds before connecting the Webre separator to ensure that fluid flow is not restricted and to remove any deposits which may have formed in the sampling port or pipeline.
- After connecting the separator, close all the outlet valves (pressure gauge port (B), liquid port – D, both vapor ports F and G – in Figure 3) and allow the fluid to flow in. Open port B and compare

the pressure recorded by the portable pressure gauge attached to the separator with the well head pressure.

- To collect the steam phase, connect the wire-bound exhaust hose to the liquid sampling valve (D) and open fully the valve. The outflow should be vibrant and noisy.
- Slowly open both steam sampling valves (F and G) and open the needle valve (E) so that vapor starts flowing through the sampling ports.
- If the vapor it is not dry reduce its flow rate using the needle valve (E)
- Connect the silicone sampling hose to it to one of the steam ports (e.g. F).
- Connect wire-bound sampling hose together with cooling spiral to the other vapor sampling port (e.g. G).
- Let the steam flow through both hoses and adjust the flow rates if necessary.
- Collect steam sample into the Giggenbach bottle using the silicone tubing according to procedure
- Immerse the cooling spiral in cold water and collect the condensate sample
- After sampling close liquid (D) and both vapor sampling ports (F and G) and disconnect the exhaust and sampling hoses.
- For sampling of the liquid phase change the positions of the both wire hoses - connect the exhaust wire-bound hose from D to one of the vapor sampling ports (e.g. F) and connect the remaining sampling hose from F to D.
- Reopen valves F (fully) and D (slowly) until a suitable flow rate is obtained and allow vapor to flow through the sampling hose and cooling spiral for 10 minutes. Cooling must bring the liquid temperature down to 30°C or less.
- Collect the liquid sample according. Use filtration and other preservation techniques as necessary, depending on the components of interest.
- Register the separator temperature and pressure.
- Close the needle valve (E), vapor sampling valves (F and G) and liquid sampling valve (D).
- Disconnect the wire-bound sampling hose from the liquid sampling valve (D) and the exhaust hose from the vapor sampling port (F).
- Dismantle and clean the sampling apparatus.

2.6 Sampling during the well discharge test and data processing

In a one-day step-rate discharge flow test, typically one complete sample for analysis of liquid and steam phase is collected (Figure 1). For detailed description of well discharge flow test, reader is referred to Axelsson (2018). To collect the most representative sample of the deep aquifer it should be taken during the first step (often called 'step zero') and before the opening of the fluid flow control valve is changed. Otherwise, the well will require discharging at least 2-3 hours after the opening is changed to equilibrate allowing for complete sample collection. Additional samples of vapour for analysis of non-condensable gases (NCG; in some cases, only CO₂ and H₂S) are collected at each step, not earlier than 45-60 minutes after changing of the valve opening. Sampling of the two-phase fluid proceeds as described in sections above. It is extremely important to record the separator pressure during sampling. Ideally, the Webre-type separator pressure should agree with the measured temperature according to a boiling point curve and should be similar to the flow line pressure.

Processing of the chemical data obtained during the analyses involves determination of the deep aquifer temperature by comparing the temperatures calculated using geothermometry (e.g. Arnórsson et al., 1998; Fournier and Potter, 1982) with temperature measured at the location of the main aquifer(s). Once the aquifer temperature has been determined, the chemical and isotopic composition of the reservoir fluid is calculated from the raw data of the discharged fluid (chemical analysis of the steam and liquid) and calculated vapour fraction, using WATCH geochemical computer code (Arnórsson et al., 2007; Iceland Water Chemistry Group, 2010) or any other suitable program. The simulated reservoir fluid composition should be compared to that of neighbouring wells and if any discrepancies are observed, they should be investigated and explained. In addition, deep fluid bubble point (pressure at which boiling starts) is calculated in accordance to the partial pressures of the dissolved gases.

The NCG content of the vapour is calculated (or approximated by the sum of CO₂ and H₂S if other NCGs are not analysed) at different discharge test steps. If the power plant separator pressure is known, the NCG content is calculated both at the collection pressure and the power plant separator pressure. The NCG concentration at distinct flow valve openings is necessary among others to decide about required power efficiency of vacuum pumps used at the steam condensation stage. It also allows to calculate the possible CO₂ and H₂S emissions from a particular well which contribute to the environmental assessment of the geothermal power plant.

The calculated deep aquifer composition indicates also corrosion and scaling potential of the utilized fluid. To assess the scaling risk a stepwise adiabatic boiling of the reservoir fluid from the aquifer temperature to the plant separator pressure (if known) is simulated using WATCH code and the saturation indices of calcite, amorphous silica and other solid phases of interest are calculated at each step. Other computer codes can be used for calculating the mineral saturation indices e.g. the PHREEQC computer code (Parkhurst and Appelo, 1999). The main advantage of this program is that it includes a wide range of thermodynamic data needed for simulations. The pitzer.dat database available together with the software is more suitable for high salinity waters than the WATCH database as it uses better method for calculating activity coefficients at high water ionic strength. It also contains thermodynamic data for additional chemical species such as CaCl⁺, which are crucial for calcite saturation state calculations in high salinity waters. It also predicts the saturation state of the fluid with respect to several mineral phases which are not included in the WATCH. The PHREEQC code can simulate conductive cooling, but not adiabatic boiling. The solution for this disability is to insert the chemical composition of the fluid at different boiling steps obtained from the WATCH and use it as an input for PHREEQC. Additionally, the PHREEQC can perform reaction path calculations, such dissolution or precipitation of various mineral and amorphous phases such as clay and carbonate solid solutions.

3. TRACER TEST FLOW (TFT)

The Tracer Flow Testing (TFT) is used for accessing the well head discharge (water and steam flow) and allows to calculate the discharge enthalpy. Enthalpy and mass flow rate govern the amount of steam available from each well and therefore the energy output. Systematic TFT tests allows to monitor the discharge enthalpy in response to the production from the field, and therefore help to understand the reservoir behaviour. For example, decreasing enthalpy can indicate breakthrough of injection water or invasion of cooler groundwater. Increasing enthalpy can reveal reservoir boiling and the formation of a steam cap. In addition, enthalpy is used for the interpretation of geochemical data as it allows correcting the discharge chemical composition back to reservoir conditions what is especially useful in excess enthalpy wells.

The TFT procedure has been used for routine measurements of wells output in operating geothermal fields (Lovelock, 2001). It is non-invasive method as it allows mass flow and enthalpy monitoring without using conventional wellhead separators and it is performed during the well production, what decreases the operational costs in general.

3.1 Sampling and analysis procedure

Tracer flow testing involves the quantitative injection and dilution of small amounts of chemical tracers mixed together (one for steam and one for liquid) in a pipeline connected to the production well-head (Figure 5 and Figure 6). Traditionally this has been done using dedicated wellhead separators or by taking wells out of production and by-passing the discharge to a total-flow atmospheric silencer (Lovelock, 2001). The flow of each phase is calculated by measuring the dilution of chemical tracers, which are injected into the flow line using an injection needle. Care has to be taken to select the appropriate tracers according to their chemical composition and stability at temperature and pressure conditions expected during the sampling of the geothermal fluid. Often, the Na-fluorescein is used as a tracer for the liquid phase and isopropanol as a tracer for the steam phase. Both are injected into the

flow line at a constant rate and using a single chemical metering pump connected to the tracer tank and the pipeline (Figure 5). The injection rate is monitored with a digital scale. The isopropanol boils in the flow line and mixes with the steam whereas the fluorescein remains in the liquid. Since isopropanol partitions also into the liquid phase its concentration is measured in both phases.

Samples of liquid and condensate are collected a good distance away from the injection point. In most cases, the samples are collected from valves close to the separation plant. Samples are collected from two valves (Figures 5 and 6) on each flow line; one on top of each pipe and one at the bottom, for steam

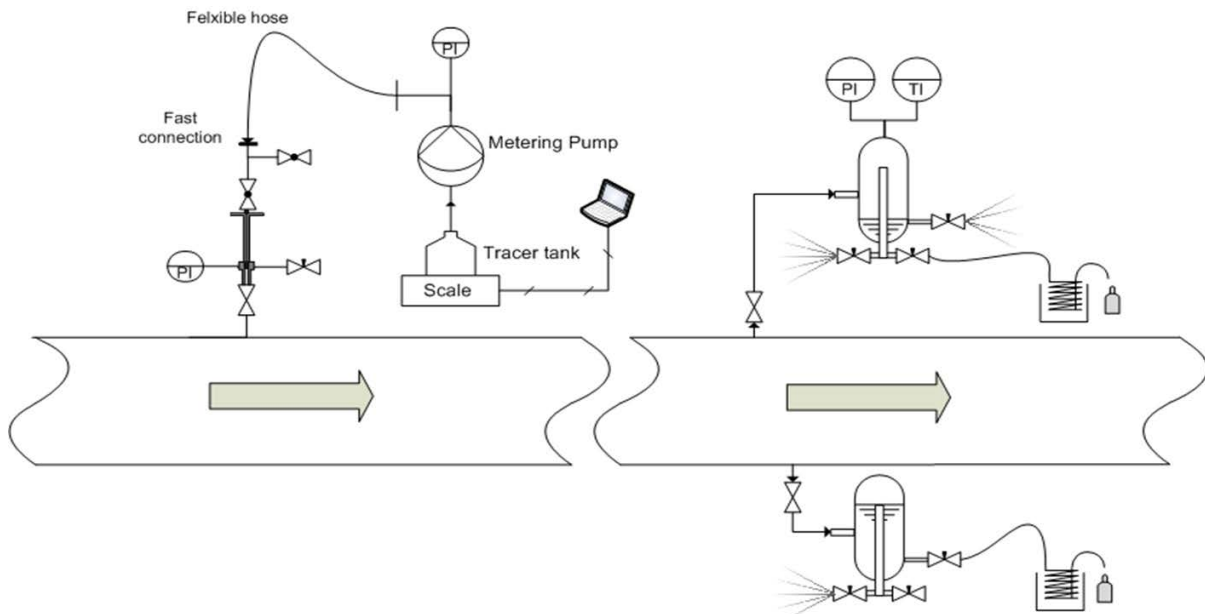


FIGURE 5: The injection and sampling set-up used during the TFT measurements (modified from Thorbjörnsson et al., 2013).

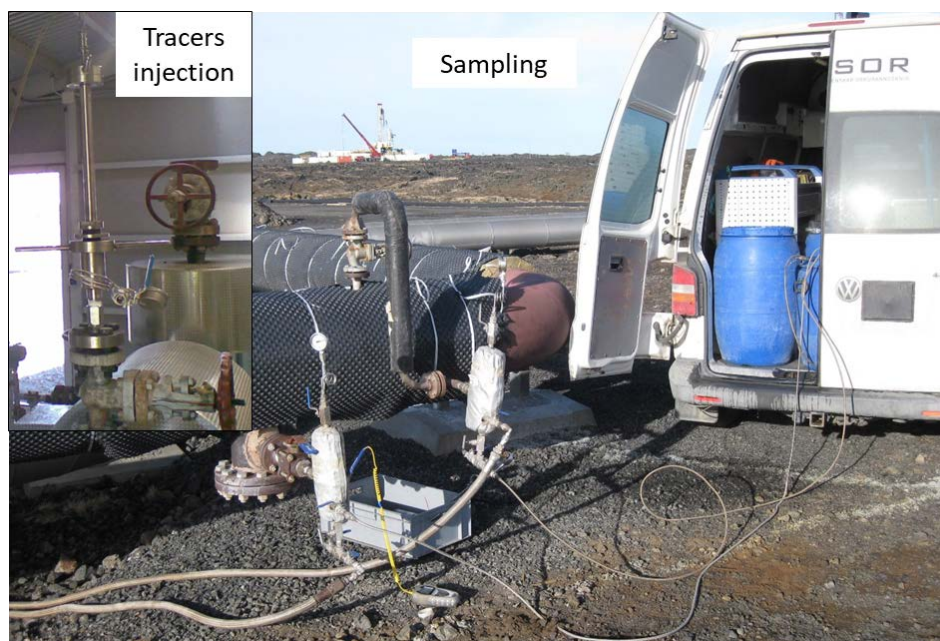


FIGURE 6: The photograph taken during the TFT measurements. Sampling is performed a good distance from sampling point. Two Webre-type separators are connected to the pipeline. Exhaust and sampling wire-bound hoses, cooling spirals (here immersed in bucket filled up with cold water), and pressure/temperature probes are also used, similar as during regular well-head sampling.

and liquid phase sampling, respectively. The Webre separators are connected to these valves and samples are collected from both phases simultaneously. The steam phase samples are condensed and cooled using a cooling spiral to ambient temperature, and the liquid phase samples are cooled to ambient temperature and diluted 1:10 with deionised water upon collection. During the sampling, the pressure and temperature are monitored on the separators.

The detailed description of this method and related mathematical formula to access the enthalpy from the data obtained during the TFT can be found in Levelock, 2001. Example of its application at the Reykjanes geothermal power plant can be found in Čypaitė et al. (2017) and references therein.

4. CONSIDERATIONS

Sampling and analytical methods used in geothermal studies have been developing throughout the years as geoscientists have been exploring geothermal areas for hot and medium temperature fluids in diverse geological settings. In addition, the improvement of laboratory techniques has made it possible to measure constituents in extremely low concentrations including isotopes, which have been recently widely used to investigate processes dictating chemical composition of the fluids. Due to increasing demand for low-cost and more efficient geothermal utilization the industry expects to direct their efforts towards hotter and/or deeper aquifers. One of the biggest challenges found in these conditions are problematic fluids – often very saline and/or corrosive. With such fluids, sampling and analytical methods need to be modified and improved to cope with difficulties arising from the physicochemical conditions at extreme depths, including extension of the thermodynamic properties of aqueous species and solid phases at high temperatures and/or salinities. Therefore, geochemists should be openminded with respect to new technologies that can be used during the sampling, analysis and computer modelling. This is crucial for understanding the geothermal systems for sustainable, efficient and long-lasting utilization.

ACKNOWLEDGEMENTS

This short manuscript summarizes shortly sampling and analytical methods developed throughout decades of geothermal exploration, development, and production in Iceland and abroad. I would like to thank all the co-workers at ÍSOR and at the University of Iceland who broaden my knowledge in this discipline.

REFERENCES

- Arnórsson, S. (ed.), 2000: *Isotopic and chemical techniques in geothermal exploration, development and use. Sampling methods, data handling, interpretation*. International Atomic Energy Agency, Vienna, 351 pp.
- Arnórsson, S., Andrésdóttir, A., Gunnarsson, I., and Stefánsson, A., 1998: New calibration for the quartz and Na/K geothermometers – valid in the range 0-350°C (in Icelandic). *Proceedings of the Geoscience Society of Iceland Annual Meeting, April*, 42-43.
- Arnórsson, S., Bjarnason, J.Ö., Giroud, N., Gunnarsson, I., and Stefánsson, A., 2006: Sampling and analysis of geothermal fluids. *Geofluids*, 6, 203-216.
- Arnórsson, S., Stefánsson, A., and Bjarnason, J.Ö., 2007: Fluid-fluid interaction in geothermal systems. *Reviews in Mineralogy & Geochemistry*, 65, 229-312.

Axelsson, G., 2018: Geothermal well testing. *Papers presented at "SDG Short Course III on Geothermal Reservoir Characterization: Well Logging, Well Testing and Chemical Analysis"*, organized by UNU-GTP and LaGeo, Santa Tecla, El Salvador, 30 pp.

Ármansson, H. and Ólafsson, M., 2006: *Collection of geothermal fluids for chemical analysis*. Iceland Geosurvey – ÍSOR, report ÍSOR-2006/016, 16 pp.

Čypaitė, V., Hardardóttir, V., Jónsson, S.S., and Thorbjörnsson, D., 2017: *Reykjanes power plant. Tracer flow testing of production wells in October 2017*. Iceland GeoSurvey – ÍSOR, report ÍSOR-17093, 21 pp.

Ellis A. and Mahon W.A.J., 1977: *Chemistry and geothermal systems*. Academic Press, New York, New York, United States, 392 pp.

Fournier, R.O. and Potter, R.W., 1982: A revised and expanded silica (quartz) geothermometer. *Geothermal Research Council Bulletin*, 11, 3-9.

Galeczka, I. and Óskarsson, F., 2019: *Reykjanes production field. Geochemical monitoring in 2018*. Iceland GeoSurvey – ÍSOR, report ÍSOR-2019/005, 91 pp.

Iceland Water Chemistry Group, 2010: *The chemical speciation program WATCH*. ÍSOR – Iceland Geosurvey, Reykjavík, Iceland, 9 pp. Web: http://en.isor.is/sites/en.isor.is/files/download/watch_readme.pdf

Lovelock, B.G., 2001: Steam flow measurement using alcohol tracers. *Geothermics*, 30, 641-654.

Óskarsson, F. and Ármansson, H., 2017: Geochemical methods in geothermal surface exploration. *Papers presented at "SDG Short Course II on Exploration and Development of Geothermal Resources"* organized by UNU-GTP, GDC and KenGen, Naivasha, Kenya, 12 pp.

Parkhurst, D.L. and Appelo, C.A.J., 1999: *User's guide to PHREEQC (Version 2) — a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. U.S. Geological Survey, Water-Resources Investigations Report 99-4259, 312 pp.

Thorbjörnsson, D., Kristinsson, B., and Ingólfsson, H., 2013: *Reykjanes power plant. Tracer flow testing of production wells in spring 2013*. Iceland GeoSurvey – ÍSOR, report ÍSOR-13089, 12 pp.