

Concept for performance characterisation of the target area

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Version 4

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Executive summary

Reservoir characterisation and monitoring methods that have been practiced in Los Humeros superhot geothermal system include (i) geological & structural mapping, namely pyroclastic stratigraphy, physical volcanology, morphostructural mapping and GIS 3-D visualization of surface and subsurface data, (ii) field geophysical surveys and in particular, magnetic, magnetotelluric (MT), gravity, passive micro seismicity and interferometric synthetic aperture radar (InSAR), (iii) field geochemistry evaluating hydrothermal alteration, geothermometers, geobarometers, pH, etc., (iv) sample analysis by X-Ray diffraction (XRD), scanning electron microscopy (SEM), petrography (PETRO) and electron microprobe analyser (EMPA), (v) fluid production monitoring of wellhead temperature & pressure, production & reinjection mass flowrates, production specific enthalpy, separated liquid chemistry, gas content of the steam and δ18O and δD isotopes, as well as tracer testing using 2,6-NDS liquid-phase tracer.

Two new, advanced seismic methods for characterisation of the deep part of Los Humeros superhot geothermal system are proposed.

The first one is reverse VSP (RVSP) by seismic while drilling (SWD) using the drilling noise. The method is known since several years, and recent improvements have been demonstrated. Invoking the reciprocity principle, thanks to the reciprocal (or reverse) geometry with the source at the bit and the receivers at the surface, or in other wells (crosswell), the method can be potentially used also at high temperatures of the drilled formation.

The second approach is the use of fibre optic distributed sensing systems. In this case the receiver is in the borehole, but it can be used also at the surface, and the sources are at the surface (active seismic sources) and also they may be passive in the subsurface (micro seismic sources). This recording technology utilizes the optical signals created by a laser interrogator and transmitted and scattered through the fibre line. This makes it possible to create an array of distributed sensors for acoustic and seismic monitoring (DAS) all along the fibre. Since the system utilized in well is optical (i.e., the fibre itself), the limitation for high temperature conditions are very different with respect to that of the electronic systems, as we will see in the next sections.

Starting from detailed structural model obtained by surface active seismic, we show by synthetic examples that VSP can predict the bedrock basement below the well, in other words, estimate how much distance is required to reach the target below the drilled depth. The borehole seismic tool (VSP) is of paramount importance for the evaluation of the geophysical information at depth, with direct time-depth calibration of subsurface structures at the well. For this reason, in the absence of legacy borehole seismic data, SWD and DAS methods have been evaluated for VSP application in SHGS systems. Both these methods are more robust in relation to high temperature conditions than conventional wireline VSP, and may easily provide large 3D images at depth. Advantages, limitations and acquisition parameters have to be evaluated for the specific selected cases of real future applications.

For a full comprehension of the mobility aspects for some PHE (Potentially Harmful Elements) in geothermal soils, several factors should be taken into account. In fact, in this particular situation, the role and the influence of the "classic" pedogenetic processes are often undergoing to the strong system energy (mainly for the role played by the temperature and pH in chemical processes), and for the abrupt/rapid chemical changes of the environmental conditions affecting these soils.

Fast secondary minerals formation, such as Fe- Oxy/Hydroxides or organic compounds, characterized by a high complexing capacity towards some positive charge ions as Pb, Cu and Zn, take place. Otherwise, when subjected to redox and pH changes, these elements can be released because of mineral solubilisation.

A consequence of the chemical-physical transformations is the total and/or partial breakage of the chemical bonds between metals and minerals to which they were previously associated. Breakage causes their release into the environment and makes them available to participate in a new biogeochemical cycle. The primary factors influencing the steam-heated acid sulphate alteration of the geothermal deposits are the redox state of the "system" (oxidation front extension), the acidic supply, the pH value of the medium, and the extent of reactions.

Selective dissolutions, namely Sequential Extraction Procedures (SEP), are useful techniques to obtain this information and, in particular, to study the minerals phases that could be responsible for the metal scavenging pathways as for Fe and Mn Oxy-hydroxides. SEP represent a suitable approach to understand metals speciation in relation to a specific extractant and extraction procedure adopted and, for this reason, are recognized as procedures operationally defined. These procedures have been applied, for comparison, on surface soils samples from two geothermal areas. The first, Los Humeros, in Mexico, and the second in Italy, from the Phlegraean Fields geothermal area. The aim was to test a suitable procedure able to describe and compare the mobility of PHE in different geothermal condition in spite to suggest an easy method to be utilized in similar environmental condition worldwide.

The sequential extraction procedure applied on the geothermal soils from Los Humeros and the Phlegraean Fields have evidenced many similarities. In fact, the mobility of some PHE elements is generally low with some exceptions. The tendency for most of the chemical species is to accumulate in the residue suggesting a strong association to soil main component. Therefore, any direct hazard to the environment as possible mobilization of some PHE can occur if the actual physical-chemical soil condition will remain stable.

With this study we have demonstrated that the SEP can be applied in different conditions by providing practical indications for understanding and managing some environmental problems related to the exploitation of geothermal energy also through EGS technology.

Last, but not least, guidelines on how to perform field tests with a new tracer stable in high temperatures are drafted. The new tracer is the inorganic anion perrhenate (ReO_4^{-}) of Rhenium, e.g. ammonium perrhenate (NH_4ReO_4), which during flooding experiments with basalt at 375°C, showed no sign of reduction of the Re recovered in the eluted fractions.

As for the ultimate characterisation of the deep reservoir in Los Humeros a >3 km deep well is necessary, corrosion mitigation aspects, materials and testing suggestions are presented in the annex. Superhot geothermal wells deliver highly more corrosive and abrasive fluids than standard high enthalpy wells, due to entrained acid gases (HCl and HF) and silica, while non-condensable gases are in much less concentration. Key challenges for the new superhot well are to demonstrate reliable long term fluid treatment and steam purification methods, as well as testing new corrosion resistant materials and equipment for operation at extreme temperatures & pressures.

1 Introduction

1.1 Objectives

The objectives of this work are to:

- Identify state of the art and propose new evolving geophysical methods for characterising and monitoring the deep part of Los Humeros superhot geothermal system when it is drilled
- Propose procedures to evaluate and monitor potential direct hazard to the environment as possible mobilization of some Potentially Harmful Elements, providing practical indications for understanding and managing related environmental problems that may arise from the exploitation of superhot geothermal systems
- Draft guidelines for the application of a new tracer stable at the deep superhot environment of Los Humeros
- Address design specifications and potential requirements for surface loop configuration and testing of a deeper superhot well when it is drilled.

1.2 Methodology

Firstly geological, geophysical, geochemical, production and reservoir testing and monitoring methods that have been or are currently being applied in characterising and monitoring the Los Humeros geothermal reservoir are analysed, also discussing their application to the deep superhot part of the system, when it is drilled and exploited.

Secondly newly introduced and currently under development geophysical methods are suggested for the future characterising and monitoring of the deeper part of the Los Humeros system, which can be coupled with, but not limited to the drilling of the first deeper well.

Thirdly, innovative procedures are developed and tested, as a new method towards monitoring soil pollution during the exploitation of the deeper superhot part of Los Humeros geothermal resource.

Fourthly, a new tracer stable at superhot temperatures, is proposed for reservoir testing of the deep part of Los Humeros, when the first deep well is drilled, and related procedures are drafted.

Finally, in the annex, surface loop configurations, and tests of new materials and steam purification methods associated with the exploitation of superhot geothermal fluids are discussed.

1.3 Limitations

Limitations of the discussed methods are analysed in the relevant chapters.

1.4 Document structure

Following this introduction, state of the art reservoir characterisation and monitoring methods are discussed in chapter 2, recommendations on vertical seismic profiling (VSP), seismic while drilling (SWD) and optical fibre DAS monitoring are drafted in chapter 3, the sequential extraction procedures (SEP) are proposed in chapter 4 as a method to evaluate the mobility of potential harmful elements (PHE) in different geothermal conditions applied on the geothermal soils of Los Humeros and the Phlegraean superhot geothermal fields, the application of a new tracer for superhot geothermal environments is analysed in chapter 5, followed by the conclusion, while the aspects of surface loop, materials testing and steam purification methods suitable for the fluids produced by superhot geothermal wells are presented in the annex.

2 Geophysical characterisation and monitoring methods in Los Humeros superhot geothermal system: state of the art

by Dimitrios Mendrinos, Christos Kalantzis, Constantine Karytsas, CRES

2.1 Introduction

Superhot geothermal systems are of paramount importance in the field of sustainable forms of energy, as they are capable of providing much higher power generation than high enthalpy geothermal fields currently under exploitation and appear to have great potential which waits to be tapped when the necessary technological advances mature. Los Humeros is such a superhot geothermal system, as some of its production wells deliver superheated dry steam and temperatures of 400-500+ $^{\circ}$ C are expected at depths >3 km.

The Los Humeros superhot geothermal system is located in the eastern part of the volcanic zone of Mexico ca 180 km NEE from the city of Mexico, at an altitude of 2,750-3,000 m. Its first ca 2 km deep well was drilled in 1982 and the utilization of the upper 1.5-3.0 km of the system started in 1990 with the installation of the first 5 MWe geothermal power generating unit [1]. Since then, more than 60 wells were drilled and additional units of 5 and 25 MWe each were installed, reaching a total installed capacity of ca 95 MWe.

Existing deep wells tap the upper two geothermal reservoirs encountered at Los Humeros. The upper reservoir is liquid dominated with temperature 300-330 °C located in augite andesite at 1.2-1.8 km depth, while the deeper is vapour dominated with high steam saturation and 300-400 °C temperature located in basalts and hornblende andesite at 1.9-2.7 km depth [2]. According to the results of the GEMex project, these reservoirs are characterized by fracture permeability. At deeper levels, within the carbonate basement, which comprises mainly of marbles of very low porosity and matrix permeability with intercalations of basaltic dykes and skarns, fluid movement of higher temperature is anticipated only within the fault zones [3].

This paper reviews reservoir monitoring methods currently practiced in Los Humeros superhot geothermal system. They aim at assessing geothermal resources in the reservoir, imaging subsurface structures, understanding the chronology of volcanic processes, quantifying fluid flow, heat transport and water-gas-rock interaction, monitoring fluid production parameters and defining reservoir flow patterns. Detailed achievement of the above will help in a deterministic approach and more accurate interpretation of the exploitation potential of the geothermal system. Methods for achieving these goals include geological & structural mapping, field geophysical surveys, field geochemistry, fluid production monitoring and tracer testing.

2.2 Geological & structural mapping

In the context of improving understanding of the geothermal and magmatic system, geological and structural mapping methods and techniques are applied to develop a conceptual model for the area. They are evaluation of pyroclastic stratigraphy, physical volcanology, which includes high-precision geochronological methods (C¹⁴, Ar⁴⁰/Ar³⁹, U-Th/zircon, U-Th/He thermochronometry and paleomagnetic dating), electron probe microanalyzer and isotope ratio measurements, (which provide valuable information about the thermal and chemical evolution of the magma chambers), methods of

morphostuctural mapping such as remote sensing & field verification, estimations of volcanic vents and heat flow and rainfall, also methods of X-ray micro-tomography, which stepwise improve the conceptual model including the permeability distribution and, visualization of surface and subsurface data (GIS 3-D). This information is important, as it provides the matrix, the boundary and the initial conditions of the system reservoir model which is subsequently used for modelling field exploitation and predicting its future behaviour and ability to deliver the steam needed for the power generation.

Above analysis has been implemented starting with surface data and followed by analysis of cuttings and cores from deep wells. The geologic and structural model of Los Humeros has been recently updated by the results of the GEMex project, according to which the superhot geothermal system includes the three main reservoirs mentioned above, which are exploited within the Los Humeros caldera boundaries.

A previous view was that caldera boundary faults isolate these reservoirs from regional lateral recharge; following this assumption recharge is limited to local rainfall [2], reinjected fluids and steam rising through basement structures.

Additional GEMex results indicate that a regional hydraulic recharge has to be taken into consideration, whereas the extension of the geothermal field may hint on the heat flow focussing effect of caldera boundary faults. According to GEMex findings, faults in the system are the result of the regional tectonic setting and the local caldera forming processes. From studies within Task 4.3 on hydrogeological data, a regional recharge through the regional faults cannot be ruled out and might be substantial. A system confinement to the caldera boundaries is not certain, although probable due to the location of the heat source.

Concerning the geologic evolution of the system, after rhyolitic dominant volcanism with episodic dome formation during 693-270 kyr ago, the 18 km in diameter Los Humeros caldera collapsed 164 thousands years ago. 69 kyr ago the smaller Los Porteros caldera, 9 km in diameter, was formed inside the Los Humeros one. Since then there have been 6 volcanic eruptions, the last of which was dated as 2.8 thousand years old. [4], [5], [6].

As only the upper part of the carbonate basement has been drilled by a few of existing deep wells, the geologic and structural model of Los Humeros can only be reliably updated by core samples taken in deeper wells (>3 km) that may be drilled for exploration and/or exploitation of the deeper superhot part of the system.

2.3 Field geophysical surveys

Field geophysical surveys commonly practiced in geothermal exploration and monitoring exploitation include magnetotellurics (MT) and microgravity surveys to locate and characterize shallow and deep structures, micro-seismicity surveys to locate active faults through which thermal fluids flow, thermal remote sensing, and InSAR (Satellite Interferometric Synthetic Aperture Radar) techniques to detect anomalies at the ground surface associated with hydrothermal processes at depth and to improve the conceptual model of the geothermal field.

2.3.1 Magnetotelluric (MT) and Transient Electro-Magnetic (TEM)

The first Schlumberger resistivity and MT surveys carried out in Los Humeros were during field exploration in the early 1980's [7]. During the GEMex project, coupled Magnetotelluric (MT) and Transient Electro-Magnetic (TEM) soundings sharing the same locations were performed. TEM soundings were used to correct the MT data. They indicated that Los Humeros is characterized by a

three-dimensional resistivity structure controlled by the main faults including Los Porteros caldera boundaries. Considerable horizontal contrasts are evident. One of the most prominent features identified is a resistive core that domes up along one of the main faults in the region. [8]

During subsequent exploration and exploitation of the deeper part of the system MT/TEM surveys carried out at regular intervals can be used for monitoring the long term resistivity structure, which may give insights on some deep processes and changes occurring in the geothermal system during exploitation, such as the evolution of steam cap.

2.3.2 Gravity

A gravity survey was carried out in Los Humeros during the early stages of field development which showed the main features of the subsurface structure of the caldera [7]. Recent gravity studies carried out during the GEMex project were a regional gravity study coupled to a study of the magnetic field carried out by the Mexican team [9], [10] and a local gravity survey carried out jointly by the European and Mexican teams. Both yielded the density distribution beneath the surface.

For the local gravity survey, a total of 344 gravity stations were measured in two different times, indicating a density distribution controlled by faults aligned in the NE-SW and NW-SE directions. In particular N-S oriented secondary faults in the northern part of the field coincide with relatively high-density distribution, whereas the NE-SW to E-W oriented secondary faults are characterized by low-density. [11] Furthermore a lower density body was identified extending to depth beneath the caldera surface.

Additional gravity surveys using superconducting gravimeters during exploitation of the deeper superhot part of the system could provide insights on micro changes in density occurring at depth, which are associated to changes in local fluid saturation controlled by boiling, fluid production, recharge and reinjection. However, this is matter of ongoing research. Monitoring the deep parts of the system will be very challenging. Permanently installed, highly sensitive gravimeters will be needed, as well as advanced processing techniques to filter the processes occurring in the upper reservoir, which may mask the signal received from the deep part of the system.

2.3.3 Magnetic surveys

The first magnetic survey was carried out by air during the early stages of field exploration, which identified a bipolar magnetic anomaly in the central part of the Los Humeros complex [7]. During the GEMex project the Mexican team investigated the aeromagnetic data in conjunction with the gravity ones. A joint inversion of both yielded magnetism and density distribution at subsurface. A magnetised elongated ellipsoidal ball shape, ca 10 km in diameter, is evident extending beneath Los Humeros caldera from surface down to 7 km depth located between the wells and the east caldera boundary [10].

During exploitation of the deep superhot part of the system repeating magnetic surveys over time will provide information on the evolution (if any) of this magnetic body under exploitation. One of other explanations is the presence of deep iron bearing fluids.

2.3.4 Active seismic

Only one active seismic survey has been carried out in Los Humeros. It was carried out by the Compañía Mexicana de Exploraciones S.A. (COMESA) on behalf of Comisión General de Electricidad (CFE) in 1998. It comprised seismic data acquisition along four 2D reflection seismic lines using Vibro seismic sources. [12] This survey was reprocessed during the GEMex project, providing the P-wave and S-wave

seismic velocities tomography, as well as the subsurface seismic structure of the geothermal system [13].

The results of the active seismic survey are considered as very reliable in terms of defining the location and extent of the subsurface fault zones, which serve as flow passages of deep fluids and are target for both production and reinjection wells. On the other hand, the main drawback of active seismic surveys is their high costs compared to the other geophysical methods.

2.3.5 Microseismicity

Monitoring microseismicity in Los Humeros has been carried out by CFE since 1994 with an installed permanent network of 6 seismographs. Most hypocentres of observed microseismic activity are located within the two upper permeable horizons of augite andesite and hornblende andesite and are associated with the reinjection fluid flow patterns due to fractures opening by contraction of cooling rock. That way, zones of high permeability have been identified, which were set as targets for subsequent production wells [14].

During the GEMex project, 20 short-period plus 25 broad-band three-component sensors were installed and local micro-seismicity was monitored for ca 1 year [13]. Location of hypocentres indicated strong association with reinjection practices. Travel-time tomography allowed the calculation of 3D P-wave and S-wave seismic velocity [13], [15] and rock moduli distribution [16], which was compared with synthetic models [17], in an effort to identify the seismic signature of a superhot geothermal system and examine potential relations to fluid properties of saturation, pore pressure and temperature. Ambient seismic noise correlation methods provided the 1-D seismic velocities profile to great depth.

During exploitation of the deep part of the system, a permanent network of seismographs would provide at low cost continuous information on local micro-seismic activity, analysis of which will provide insights on important reservoir processes, such as fracture permeability evolution, recharge flow patterns and fluid thermal properties.

2.3.6 Remote sensing techniques

The InSAR remote sensing synthetic aperture radar satellite images taken by the ENVISAT satellite of the European Space Agency (ESA) during 2003-2007 have used to generate digital maps of surface elevation and monitoring subsidence and structural stability of Los Humeros caldera [2].

Processing of these data during the GEMex project, identified subsidence of max 8 mm/y at the north part of Los Humeros caldera surface, which were related to fluid volume changes in the reservoir. Furthermore, C-Band radar images from Sentinal-1 ESA Copernicus satellite were used to map the deformation caused by the reinjection induced Mw 4.2 earthquake of 8 February 2016, which highlighted the activation of shallow faults (max 1.2 km depth) beneath the caldera. [18]

Differential GPS surveys carried out every six months identified horizontal ground displacements of 3 cm in NW-SE direction during a large earthquake, indicating that the caldera is tectonically active. The GPS surveys will continue for the next years. [18]

2.4 Geochemical analyses

Geochemical analyses include geochemical characterization of hydrothermal fluids and rocks including geothermometers, geobarometers and pH, geochemical and petrographic characterization of volcanic rocks, fluid inclusions and hydrothermal alteration, as well as x-ray tomography of reservoir rocks from

core samples to determine the porosity and permeability. Tools to accomplish this are sample analysis by X-Ray diffraction (XRD), scanning electron microscopy (SEM), petrography (PETRO) and electron microprobe analyser (EMPA).

In Los Humeros, field-based petrological and thermo-barometric analysis of the post-caldera surface lavas was carried out during the GEMex project, which pointed to a revised deep system conceptual model comprising of multiple magma chambers within the carbonate basement at 3-30 km depths, where the main basaltic magma reservoir is expected. Thermo-barometer models indicated rock melting and mineral forming at 900-1250 °C. [19]

Oxygen isotope data of skarn minerals and fluid inclusion analysis of rock samples from the Las Minas fossil geothermal system, which is adjacent to Los Humeros, highlighted the typical evolution of a magmatic-hydrothermal system characterized by an early hypersaline fluid (18-60 % NaCl equiv.) of very high temperature (500-650°C) circulating within fractures, which emanated from a crystalizing melted magma, and the presence of a vapour phase produced at hydrostatic pressure of 40-1000 bar. [20]

During drilling the deeper superhot part of Los Humeros, analysis of fluid inclusions within core samples would update clues concerning the chemistry and temperature of paleo fluids, which is the maximum temperature expected to be encountered at deeper levels. Thermo-barometric analysis would update the conceptual model of the deep system, which is essential for the definition of drilling targets for the production and reinjection wells, and setting the initial conditions in a transient numerical model of the superhot system evolution.

2.5 Fluid production parameters

In Los Humeros, since production started in early 1980s, fluid production parameters monitored are wellhead and well-bottom temperature and pressure, production and reinjection mass flowrates, production specific enthalpy, steam saturation, separated liquid chlorides content and chemistry, gas content of the steam and δ 18O and δ D isotopes. Since reinjection practice started, reinjection mass flow rate was recorded. During 1982-2012 ca 123 Mtons of fluid were produced comprising ca 84% steam and ca 16% liquid, only 5% of which was reinjected. This massive fluid extraction from the reservoir with very limited reinjection resulted in the following changes to occur within the reservoir: pressure decrease, enthalpy and vapour saturation increase, boiling with steam condensation, production of reinjection returns heated to reservoir temperature and deep steam recharge. [1]

Continuous monitoring of above parameters is essential in order to foresee changes in produced energy and plan further production and reinjection wells, as well as future power plant expansions.

2.6 Tracer testing

Tracer testing applications have as an objective the evaluation of wells interconnectivity by tracer injections at one reinjection well and the return of tracer in production wells, which provides valuable insights of the geothermal system. High temperature resistant 2,6-NDS liquid-phase tracer has been practiced in Los Humeros, by adding it to the reinjected fluid. The results revealed reinjection returns in all monitored production wells, corresponding to 1% of injected fluid. The conclusion is that 99% of injected fluid flows to the deep part of the system and that no thermal interference is expected. [21]

Further tracer tests with new tracers resistant to superhot fluids encountered at depths beneath 3 km in Los Humeros, together with continuing tracer input in reinjection wells will provide additional information on the deep flow patterns that will affect geothermal energy production, as reinjection practice expands and exploitation of the deep superhot part of the system commences.

2.7 Reservoir modelling

Reservoir modelling practiced in Los Humeros employs numerical models of fluid flow and heat and mass transport (OpenGeoSys and FEFLOW) to quantify rates of heat transport from source to surface, thermophysical and chemical properties of produced fluids [2]. When only wellhead production data are available, a wellbore simulator (e.g. WELLSIM) can be employed to calculate bottomhole transients.

During the GEMex project the SHEMAT and TOUGH-2 heat and mass transport reservoir simulators were used in order to model the natural state of the Los Humeros reservoir, using all data collected and the results produced by the project consortium. One of the simulation results was that temperatures of ca 400 °C are expected at 3 km and above 500 °C are expected at 4-7 km depth beneath the caldera. [22], [23]

During production, reservoir modelling is imperative in order to predict the changes of thermal, physical and chemical properties of the reservoir fluid during exploitation, and the ability of the reservoir to deliver the necessary geothermal energy, which is needed in order to take important decisions on future exploitation and development of the geothermal system for power generation.

2.8 Conclusion

All above technologies, techniques and methods are greatly contributing to significantly improve our knowledge of the features and capabilities of the geothermal field and to make optimal decisions about its current and future exploitation.

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3 Seismic evaluation & planning SHGS monitoring for reservoir characterization

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3.1 Introduction

This chapter describes the contribution of OGS, which has the target to make recommendations for innovative borehole technologies and methods that can provide information at depth to characterize super-hot geothermal systems (SHGS), in particular for the Los Humeros caldera site studied in the framework of GEMex project. Geophysical aspects analysed and reviewed this activity include:

- 1. Recommendations on vertical seismic profiling (VSP)
- 2. Seismic while drilling (SWD)
- 3. Optical fibre DAS monitoring

For this purpose we start from the analysis of the active-seismic results of Los Humeros obtained in the framework of deliverable D5.3 'Detection of deep structures' (Jousset et al., 2019), with the support of the numerical modelling performed by OGS for the geothermal area (deliverable D5.5, Poletto et al. 2019, and also D5.3), and subsequent studies with integrated interpretations of different geophysical datasets in the framework of the GEMex project.

A summary of these results and implications also for the purposes of next drilling phases are part of a contribution of OGS in the GEMex deliverable D8.1 (in preparation). In this report (D8.1) we evidence how the seismic measurements can provide information for the assessment of the geo-mechanical properties in geothermal reservoir with temperature, including melting conditions

3.2 The active-seismic model

The active seismic data of the Los Humeros caldera consist of four seismic lines, named L2, L3, L4 and L5, sub parallel and crossing each other in the local model of the LH caldera (D5.3), where a complex system of faults has been interpreted (Calcagno et al., 2018). OGS has processed these field seismic data by pre-stack depth migration (PSDM) with iterative interpretation of the seismic horizons in a first phase based on recognition of the seismic events, and in a second phase by integrated interpretation with the geology, using the data of the wells located in the proximity of the seismic lines.

The results of this processing and the related inversion driven by interpretation are not only the seismic sections in depth, but also the seismic velocity model in depth for compressional waves, together with the identification of horizons that make it possible to build a reliable velocity model for the synthetic simulation of seismic wavefields. These results have been compared with results from other methods, like the passive seismology by network of seismometers at the surface, with some differences in the trends and details for the different size of pixels used in the inversions and different resolution for detailed imaging at depth.

In particular the surface seismic section provide more detailed images of the structures in the subsurface, in this complex and faulted area. In this report we use as a relevant example the processing results of seismic line L5, which is shown in Figure 3-1 with the interpretation of the main horizons. The motivation of this choice is because this line is in the proximity of two relevant reference wells, H28

and H26, which provide information useful for the interpretation, this information is available in literature (Carrasco-Nuñez et al., 2017; García-Gutiérrez, 2009; García-Gutiérrez et al., 2001; Cedillo Rodriguez, 2000).

The maximum depths of the H28 and H26 wells from the surface is about 2570 and 2540 meters, respectively. They pass through all the pre-caldera, caldera, and post-caldera formations, and in particular the total depth (TD) of well H28 reaches the basement, which is marked by a violet line indicated by yellow bold arrows in Figure 3-1, where the well positions are shown together with the lithology maps of the encountered geology by H28 and H26. With a similar geometry, the total depth of H26 is close to the interpreted basement.

At this stage all the depth information is obtained by inversion of the surface seismic data, and by calibration by geology in the wells. The two shown wells are relevant examples, but also a plurality of other wells was used in this interpretative processing

3.3 Importance of the borehole seismic measurements

For this site location borehole seismic data, say, vertical seismic profiles (VSP), are not available. Some well logs are available at marginal positions (Figure 3-1 at the right-hand side) and limited depth intervals, so that they offer only partial limited data to support interpretation at depth. However, borehole seismic plays a key role for the seismic-time depth calibration, thus giving certain positions of the seismic and geological properties measured at depth on the seismic sections measured from the surface.

In this integrated process involving surface and borehole seismic, the typical elements are the sonic and density logs measured at depth, the seismic profiles measured in the borehole, and at the surface the seismic lines interpreted to study the reservoir. In this case we have not borehole information besides the interpreted and well calibrated sections, and the study is performed by simulating a synthetic VSP dataset based on the model of the results of Figure 3-1 and shown in Figure 3-2.

The result of Figure 3-1 show us that we can interpret the event corresponding to the basement below the caldera, which is a key information for the assessment and definition of the geothermal reservoir. So the first step of our analysis is to evaluate the observability of the VSP reflections, which depend on the contrast in the acoustic impedance. We proceed as follows.

3.3.1 Calculation of the Synthetic Seismogram (SS)

Using the velocity-depth model superimposed to the model with horizons in Figure 3-2, we calculate the reflection coefficient for compressional waves at the interface between two layers 1 and 2 as

$$R = \pm \frac{\rho_2 V_2 - \rho_1 V_1}{\rho_2 V_2 + \rho_1 V_1},$$

where V is the wave velocity, ρ is the density calculated by the Gardner's relation

$$\rho = 0.31 \times V^{0.25}$$
,

and the sign depends on the transducer type, for pressure (hydrophone) or particle velocity (geophone). The reflectivity is calculated with only the primary reflection coefficients in depth Z and in time. The position in depth of the reflection coefficient is given by the Z-V curve of Figure 3-2, the position in time is calculated at two-way-times $2 \times Z_i/V_i$ obtained in the velocity intervals for the reflections. The

reflection series in times is then filtered with the same bandpass filter 8-24 Hz used for the surface seismic. This provides the synthetic seismogram (SST), calculated for both H28 and H26 wells.

The filtered SST is then converted back (stretched) in depth, and inserted in the seismic section as shown in Figure 3-1. The deepest reflection below each well corresponds to the interpreted basement horizon. This analysis, performed after minor tuning of the velocity profile to better tune amplitudes with surrounding real data of the section split at the well positions, shows that the interpreted basement is observable from seismic point of view, is detected by reflectivity analysis and consistent with the velocity data.

This motivates the analysis by synthetic VSP calculated with the same seismic model.

3.3.2 Synthetic VSP in Los Humeros: prediction of target horizons

Among different geometries utilized for VSP, such as, walk-above, multi-offset, 3D VSP that will be considered as the proposed technologies for geothermal applications in the following of this chapter, the common and very important one enabling to provide detailed geological and geophysical calibration along the well, is the zero-offset VSP or better Near-offset VSP. The source is used at surface in a position close to the well, and the profile is shot (acquired) with many regular positions at depth, according with the sampling theory for the investigated wavefields.

This provides immediately the profile of the interval seismic velocities at depth along the well, i.e., direct velocity measurements in the intervals between sensors, not velocity estimations by remote measurements only! This is immediately provided by the picking of the direct arrivals clearly interpretable in the total field, as in Figure 3-3 where the VSP corresponds to the offset positions at -50 m from the well H28. The vertical axis of the panels is the one-way seismic time (OWT) of the seismograms, the horizontal scale is the receiver depth. The weaker reflections from layers below the receivers (upgoing reflections) have opposite slope with respect to the stronger direct and downgoing waves. Wavefield separation is applied, and the upgoing reflections with opposite slope are reinforced and become clearly interpretable (Figure 3-4). When a reflection encounters the direct arrival, the VSP receiver is in the depth position of the reflecting interface. This is a key interpretation step in the VSP processing.

It is important to note that reflections are observable below the receiver level in the well, therefore the target layers can be predicted by a VSP before reaching them. As in Figure 3-5, where the separated reflections are deterministically converted to two-way time (TWT) by adding the direct-arrival time to the reflection time, that gives the same time of the surface seismic with a good approximation. The interpreted and predicted reflection is the top of the basement. In this case, the comparison is done with the synthetic seismogram in time (SST), corresponding to the synthetic seismogram in depth (SSD) compared with seismic in depth (PSDM) in Figure 3-1.

These examples demonstrate the potential of VSP measurements to predict the target formations in next geothermal wells. In the next sections we will discuss proposed technologies to realize these measurements in SHGS wells, for near-offset VSP but not limited only to near-offset VSP.



Figure 3-1: Active seismic line of Los Humeros, line L5 pre-stack depth migration (PSDM) with interpretation of horizons. The horizon indicated by the yellow arrows is the bedrock basement. The synthetic seismograms in depth (SSD) are inserted in the line split at positions of well H28 and well H26.



Figure 3-2: Velocity model (compressional velocity) of L5, with the velocity-depth profile at H28 position as an example. This function was used to calculate the SS of well H28 (see Figure 3-1).



Figure 3-3: Synthetic VSP calculated for well H28, at offset -50 m total field. The vertical scale is time (s), one-way time (OWT). The horizontal scale is depth (m) of receiver in well. Before wavefield separation the direct arrival and downgoing waves mask the reflections from layers below (upgoing waves), with opposite slope in the Z-T panel.



Figure 3-4: Result of wavefield separation for the synthetic VSP calculated for well H28, at offset 50 m. After wavefield separation the upgoing reflections are very clear. The left panel shows the direct arrivals with downgoing waves. The right panel shows the upgoing waves after separation. When a reflection encounters the direct arrival (picking evidenced), the receiver depth is at the position of the reflecting interface.



Figure 3-5: The upgoing reflections of the VSP H28 are processed to improve the signal wavelet using the signature of the corresponding downgoing waves and converted to two-way time (TWT), i.e., the time of the surface seismic sections by adding the time of the direct arrivals to the time of the reflections, to 'flat' the horizons. In this case the VSP reflections are compared to the synthetic seismogram in TWT (SST), corresponding to the synthetic seismogram in depth (SSD) on H28 in Figure 3-1. The deeper reflection corresponds to the interpreted bedrock basement, which can be predicted in depth (blue vertical line) by projection of the time line (horizontal line) and first arrival line (red line) below the VSP depth, interrupted at shallower positions for explanation purposes. Since the model is consistent with the L5 interpretation driven by well information and velocity analysis by calculation of reflection coefficients, this example indicates that bedrock is predictable below the well with VSP measurements at distance of some hundreds meters.

3.4 Improved technologies for borehole monitoring in SHGS

Two technologies are proposed in the following for the possible utilization of VSP in super-hot geothermal wells. It is well known that the high temperature conditions, up to about 400 °C in some well in Los Humeros, make it difficult to utilize conventional wireline VSP tools because of the limitations in the electronic and wireline cable technology, which as a standard in non-geothermal conditions can operate at temperatures of the order of 150 °C. This limitation would require the cooling of the well by mud circulation, and to perform the acquisition in a limited time, with the risk of problems in case of delays, and this operation requires the presence of the drilling rig. In the absence of the rig, this method is problematic. Recently some logging tool prototypes have been developed and tested in the framework of the DESCRAMBLE H2020 project (Hjelstuen et al., 2018) for exploitation of super-critical water from deep geothermal resources, with insulated logging probe allowing to perform downhole measurements in well at high pressure and temperatures of the order of 400 °C for six hours.

To extend the applicability of VSP in geothermal wells, we discuss and propose here two approaches. The first one is reverse VSP (RVSP) by seismic while drilling (SWD) using the drilling noise. The method is known since several years, and recent improvements have been demonstrated. Invoking the reciprocity principle, thanks to the reciprocal (or reverse) geometry with the source at the bit and the receivers at the surface, or in other wells (crosswell), the method can be potentially used also at high temperatures of the drilled formation.

The second approach is the use of fibre optic distributed sensing systems. In this case the receiver is in the borehole, but it can be used also at the surface, and the sources are at the surface (active seismic sources) and also they may be passive in the subsurface (micro seismic sources). This recording technology utilizes the optical signals created by a laser interrogator and transmitted and scattered through the fibre line. This makes it possible to create an array of distributed sensors for acoustic and seismic monitoring (DAS) all along the fibre. Since the system utilized in well is optical (i.e., the fibre itself), the limitation for high temperature conditions are very different with respect to that of the electronic systems, as we will see in the next sections.

Obviously, the joint use of both these methods and tools is even more recommended as beneficial for geothermal applications.

3.4.1 SWD concept and method

Figure 3-6 illustrates the basic concept of the conventional drill-bit seismic technology by only surface measurements (Poletto and Miranda, 2004). In the basic approach, a reference signal (pilot) representative of the unknown and random drill-bit generate vibrations is measured on the drilling rig. Similar to Vibroseis, the pilot signal is correlated with the traces of the seismic sensors at surface or crosswell, and after some processing step applied to remove the filtering effects in the drilling plant and delay, one obtains interpretable seismograms (RVSP). Several variants can include seismic interferometry (Poletto et al., 2010) or focusing methods as beneficial in the absence of reliable pilot signals. An extensive introduction on and description of the fundamentals of this technology is given by the monography of Poletto and Miranda (2004), which shows examples of applications (SWD products) not only for near-offset VSP, time-depth calibration and prediction ahead of the bit ahead total depth (TD) while drilling, but also for imaging in 2D and 3D including crosswell with anisotropy analysis. This technology has been and is still used by Oil & Gas industry.

More recently, SWD has also been used for geothermal applications, to provide seismic information in addition to existing gravity, electric and electromagnetic (EM) surveys. Results obtained in a Nevadawell survey have been discussed by Poletto et al. (2011). The characterization of the faulted area by SWD was in agreement with the post drilling analysis of well results, and imaging of fractures was investigated by tomographic inversion of seismic results, but also by analysis of full-waveforms recorded in the field with the tuning of the related seismic model. Note that this is a "full-waveform analysis" rather than a "full-waveform inversion" which would require more detailed physical information. The study demonstrated that it is effective in a complex faulted area, as shown in Figure 3-7, were a real field shot of the drill-bit signal recorded during a geothermal survey is compared to the 'fault response' (diffraction) given by the difference of the synthetic signals calculated in model with and without fault (Poletto et al., 2011).

Finally, we have to mention important recent improvements in SWD by downhole recording of reference signals (Poletto et al., 2014; Poletto et al., 2020), as shown in Figure 3-8, which describes the use of downhole reference (pilot) tools and shows improved results of high quality as shown in Figure 3-8 (right side). The novel approach includes the use of the drill-bit ground force to recover the far-field radiated source signal (Poletto et al., 2020).

For all these reasons, and thanks to improved technology by tools and large receiver arrays, we underline the potential importance of this technology which provides at the same time large array of source points at depth (bit positions in the well without limitations for temperature!) and large array of surface receivers, easily usable at the surface with many recording points and large offsets, including 3D geometry.

3.4.2 Synthetic RVSP SWD examples for Los Humeros

In addition to the near-offset VSP examples shown for prediction and time-depth calibration purposes in Figure 3-3, Figure 3-4 and Figure 3-5, we simulate using the same velocity model, synthetic shots with arrays of offset traces at the surface and the drill-bit source at depth. For this purpose, we use vertical geophone components at the surface and a vertical force at the bit. These results are calculated by the full-waveform elastic code already used for the near-offset VSP examples and described, e.g., in the deliverables GEMex deliverables D5.3 and D5.5 (Poletto et al., 2019). The pixel dimension is 10 m, and the source central frequency 15 Hz.

The synthetic shots are calculated both in well H26 and H28 at depth 2500 m from surface level. Figure 3-9 shows the schematic representation of the model with three shot points (red stars) in well H28. In Figure 3-10 we compare the SWD shots at 2500 depth in wells H26 (on the left side) and H28 (on the right side). The depth is close to the maximum well's depths. We observe the difference in the signals that can be interpreted in these field-shot signals as related to important variations in the subsurface, in the complex area due to the presence of faults and also of near-surface variations in the different zones of the caldera. This can be considered as a very important information coming from the source at depth, that can be used with an approach similar to the approach proposed by Poletto et al., 2019 (Chapter 2 in the GEMex deliverable D5.9, Wheeler et al., 2019).

Advantage of the SWD method is that this information can be in principle obtained at close intervals at all the depth levels of the well, depending on the signal quality related to the drilling conditions and parameters (Poletto and Miranda, 2004). Figure 3-11, shows as an example two more shots of H28 at depth levels 900 m and 1700 m in addition to the shot at 2500 m shown in Figure 3-10 right side. In this case the variation in the signal is related only to the depth of the bit. All these data can be repeated at regular depth intervals (e.g., every 10 meters) to provide a lot of precious information in the subsurface for inversion of arrivals (traveltime tomography), processing of reflections (migration) and imaging, as well as full-waveform analysis, e.g., to identify diffractions from faults.

Finally, it has to be underlined that large part of this information can be obtained while drilling, for example the prediction to evaluate if the basement target is expected to be close or not to the total depth (TD) of the well.



Figure 3-6: Seismic while drilling (SWD) by drill-bit source, basic concept and method (modified after Poletto and Miranda, 2004).



Figure 3-7: On the left side, example of SWD RVSP field shot versus offset acquired using the drill-bit source and a 2D surface line of seismic receivers in a geothermal survey in Nevada (Poletto et al., 2011). The interpretation of these full-waveform signals before VSP processing indicates that the subsurface below the left-side branch of the line is very different from the subsurface below the right-side branch of the receiver line extended around the well. At the right side of the shot the complexity of the signal is interpreted as due to the presence of a fault system (confirmed by the well results): The panel at the right side of this figure shows the calculated fault response, as difference of the synthetic signals in the model with fault and without fault. The agreement of this analysis of full waveform in the SWD shots with the real data is remarkable.



Figure 3-8: Example of improvements in the SWD technology using downhole measurements, in this case in the crosswell geometry (scheme at the left side). The quality of the SWD signal is shown in the right-hand side figure (after Poletto et al., 2014).



Figure 3-9: Active-seismic model of Los Humeros, line L5. Equivalent to a walkaway VSP with wireline geometry using the source at surface and receivers in well (figure in the small box), shots of SWD revers VSP (RVSP) are simulated with the drill-bit seismic source in well and receivers at the surface, as schematically shown by the figure. Three shots are calculated at the positions of the red stars in well H28, at well depths 900 m, 1700 m and 2500 m from the surface. One shot is also calculated in H26 at 2500 m (the star is not shown in figure).



Figure 3-10: Comparison of seismic while drilling (SWD) synthetic shots calculated with the source at 2500 m depth in wells H26 (left side panel) and well H28 (right side panel). The horizontal dimension is the distance at surface. Due to the complexity of the caldera area in the subsurface but also at the shallow surface, the shape of the shots is different, depending on and conveying information on local recording conditions.



Figure 3-11: For comparison with previous results, SWD synthetic shots in well H28, with the drill-bit seismic source at depths 1700 m (left panel) and 900 m (right panel).

3.4.3 DAS by fibre optic

Fibre optic technology for distributed acoustic sensing (DAS) is a relatively recent technology with widespread applications in the field of downhole monitoring and also surface monitoring. Together with acoustic measurements, the fibre can provide also distributed temperature monitoring (DTS), and is also used to measure flow in wells and in some cases strain.

Figure 3-12 illustrates the concept and method of DAS. When a laser launches a light pulse in an optic fibre, the in-homogeneities in the fibre create backscattered events, which are recognized by the optical reflectometer at the input side of the system. The axial distance position x of these signals along the fibre is calculated knowing the light speed c, of the order of 200.000 km/s, in the optic fibre and measuring the time t_0 of the back scattered signal, as

$$x = \frac{ct_0}{2}.$$



Figure 3-12: DAS concept and method

When the fibre is subject to a perturbation, as when a seismic wave hits the fibre, the consequent contraction or extension of the fibre creates a difference in the phase of the signals associated to the selected scattering position. Making the difference at selected investigation distance between points, distributed at regular intervals along the fibre creates an output as an array of sensors usable for geophysical monitoring. In other words, each point of the fibre at selected intervals can be used as an acoustic sensor.

The parameters (gouge length and pulse duration) used to calculate local phase differences determine the resolution and the sensitivity of the system to axial perturbations with different apparent wavelengths. The native output of DAS at each recording position is in most of cases the strain rate

$$s(x,t) = \frac{\partial}{\partial t} \frac{\partial u(x,t)}{\partial x},$$

where u(x, t) is the axial displacement. The DAS sampling in space can be typically also very dense, with acquisition receiver intervals of the order of fraction of meter, e.g., also 0.5 m or less. The length of the fibre can be also of several, also tens, kilometres. The frequency of the signal can range from a fraction of Hz to thousands Hz.

All these characteristics together with the low cost of the installation of this thin distributed transducer (the fibre itself) compared to conventional borehole or wireline arrays, make this tool very convenient, and sometimes usable as the only solution, so that in the recent years it was used in many monitoring and borehole applications.

Several installation solutions are utilized in boreholes:

- 1. Cemented outside the casing
- 2. Installed on internal pipe lines
- 3. Lowered in the well in the logging mode (by natural leaning against the wall of the well)
- 4. To measure acoustic waves in fluids.

These solutions have decreasing effectiveness from the top to the bottom. Permanent or retrievable solutions can be adopted, the former for time lapse applications.

The technology here summarized was improved in the recent years, thus providing better signal quality. Even if gaining from availability of dense distribution of sensors, compared to conventional geophone, the standard DAS has lower sensitivity of the order of 30 dB. The large array compensate in part this shortcoming by redundancy used to improve S/N.

Moreover, while conventional geophones can provide 3-C component, a straight DAS fibre essentially provides the axial component, with azimuthal symmetry, with a sensitivity to strain wave varying as $cos^2\theta$, where θ is the incidence angle between the wave and the fibre, i.e., the sensitivity is maximum when $\theta = 0$ that means that the wave propagation direction is axial, while the sensitivity is zero when the wave direction is perpendicular to the fibre with $\theta = 90$ degrees.

In comparison, the sensitivity of an axial single-geophone component is $\cos \theta$, so that at relatively wide and medium-wide angles the condition for a geophone is more favourable.

Nevertheless, the availability of such a large and dense array is a very advantageous condition, since it is sufficient the use of a single source position to acquire a VSP with a large number of receivers in the well. Moreover, the fibre optic technology largely improved in the recent years, in terms of signals available by processing, in terms of sensitivity relative to conventional sensors, in term of broad side response with respect to the incidence angle using special DAS helically wound cables (HWC).

Micro seismic monitoring by DAS

As a further mention, in addition to VSP, DAS also enables permanent borehole micro-seismic monitoring, especially of larger-magnitude events that originate at existing fault locations. The broad bandwidth and high dynamic range of available DAS technology enable the accurate measurement of large low-frequency seismic signals generated at existing fault locations. The technology's long array sensing aperture enables geolocation of these events in deviated wells.

Recent advancements of DAS

We mention three main aspects:

1. The first one is the capability to use the fibre dense array to recover not only strain, but also particle velocity (or equivalently acceleration) from the native output signal, together with the vibration polarity, which was lost in the native strain (or strain rate) signal. The approach is described in detail by Poletto et al. (2014). We, for example, can obtain axial particle acceleration by

$$a(x,t) = \frac{\partial}{\partial t} \int_{x} s(\eta,t) d\eta,$$

or equivalently particle velocity by $v(x, t) = \int_t a(x, \tau)d\tau$. The key point in this transformation is the robustness of the space integral thanks to the dense spatial array of receivers. As discussed by Poletto et al. (2016) these quantities, namely acceleration and velocity, when considered in pairs with strain rate and strain, respectively, are 'dual quantities', similar to dual-sensor measurements done for marine applications. It is familiar to geophysicists that the combination of the dual measurements summed and subtracted with a simple scaling factor make it possible an immediate separation of upgoing and downgoing wavefields, which is a key processing step in VSP, note, without needing to determine and pick the direct arrivals. This result will be shown in the following of this chapter for 3D VSP examples.

- 2. Sensitivity in DAS has largely improved by recent engineering solutions. This enhancement consists in the addition of impurities to the fibre, with the result of increasing the back-scattering response, and at the same time preserving the propagation at distance of the light-pulse signals. Figure 3-13 shows the comparison of conventional and engineered fibre with conventional geophones. This example demonstrates the improved quality of the enhanced DAS signals, comparable for single recording positions to conventional geophones.
- 3. The third improvement, is the enlargement of the broad side response of the cable with respect to the lateral incidence angles, which is achieved using DAS helically wound cables (HWC) instead of the straight one (for the theory see, e.g., Kuvshnikov, 2016). Demonstrated by industry for the use in shallow surface applications in trenches, the robustness for the utilization in wells would be promising for crosswell applications, but it has still to be demonstrated.


Figure 3-13: Signal quality and S/N in VSP signals by conventional DAS, enhanced (engineered) DAS, and vertical geophone Z (modified after Athena Chalari et al., WORKSHOP II - Post-Open Forum workshop organised by ENOS, San Servolo, Venice, 26th April 2018). The improvement of the response and S/N in the enhanced DAS is remarkable, and comparable to geophone.

Real 3D DAS VSP examples

As a summary of the previous discussion, the following examples are modified after Poletto et al., 2nd Workshop of ENOS Experience-Sharing Focus Groups, San Servolo, Venice, 23 April 2018. These data are part of a 3D DAS VSP acquired for CO₂ storage (CCS) monitoring purposes in the framework of the ENOS project. They represent results of the base survey before injection. A conventional linear DAS array installed in a vertical well is available for monitoring purposes. The array was set with sensors every 0.5 m in depth, from the surface to the maximum well depth of 1450 m. So, a total of approximately 3000 traces were acquired for every shot position (Figure 3-14). After quality control in field, a total of 390 shots by Vibroseis source were acquired, with good data quality also at medium large offset for the characterization of the reservoir, after appropriate feasibility study.

Figure 3-15 shows the total VSP signals acquired in the same azimuthal direction at different offset position in the 3D DAS VSP survey. With different sensitivity responses, we observe direct arrivals and also reflection and other events that will be used in the further processing.

Finally, Figure 3-16 shows the effectiveness of the proposed wavefield separation method for VSP at different offsets (distance of source from well), without needing to pick the direct arrivals in the 3D VSP dataset.



Figure 3-14: Using a single shot position, such as vibrator source at the surface, provide a complete VSP in depth by das large and dense array installed in a well. Moving then the source around the well, provides 3D DAS VSP datasets that can be processed to obtain 3D cube of images at the well. This product is important for time-lapse applications. The method gains from robust wavefield separation thanks to the dense sampling in space (short receiver intervals in the well). Examples of effective wavefield separation with real 3D DAS VSP data is shown in the next figures.



Figure 3-15: Example of DAS VSP part of a 3D survey. Each VSP panel correspond to a shot position. The VSP panels are selected at different offsets. At shorter offset, the direct arrivals are stronger. At larger offsets, the upgoing reflections are more evident (modified after Poletto et al., 2nd Workshop of ENOS Experience-Sharing Focus Groups, San Servolo, Venice, 23rd April 2018).



Figure 3-16: Examples of effective separation by 'dual method' proposed for DAS signals by Poletto et al. (2014). The results are obtained using a trace at short offset (top panels) and medium-large offset, extracted from the 3D DAS VSP dataset (modified after Poletto et al., 2nd Workshop of ENOS Experience-Sharing Focus Groups, San Servolo, Venice, 23rd April 2018). The approach is effective, without need of picking of the direct arrivals, which can be more problematic at larger offset.

DAS for super-hot (SH) borehole geothermal applications

A key aspect in this analysis is the possibility to use DAS measurement methods in hot and super-hot boreholes. General indications coming from literature and DAS industry about temperature limitations for DAS systems are:

- High temperature DAS measurements in super-hot wells are reported by Kasahara et al. (2019, 2020) at 264 °C, for the seismic approach characterization of geothermal reservoirs using DAS and full-waveform inversion (FWI). Kasahara et al. (2020) also consider the possible use of DAS at higher temperatures, of as high as 500 °C, although coating the fiber using an appropriate skin is necessary to avoid hydrogen invasion.
- It is reported that available special optical fibre coatings may range in the temperature interval $-60 < ^{\circ}C < 300$ (Polyimide).
- In literature and public information by major contractors it is reported that High-temperature wells, such as those used for steam injection, can be imaged with DAS. The process makes use of fibres that can withstand temperatures in excess of 300°C.
- It is also possible to make repeatable borehole seismic measurements safely in producer wells, injector wells, wells with restricted access and wells which are highly deviated.

This makes the DAS technology potentially applicable in several wells of the Los Humeros area at relevant depths for borehole seismic purposes.

3.5 Discussion on advantages and limitations of SWD and DAS

Both SWD and DAS methods are suitable and can be used to acquire large surveys, including 3D RVSP or 3D VSP configurations.

SWD provided the great advantage of seismic while drilling, i.e., usable for prediction of the target. The method does not suffer temperature limitations with only-surface sensors. With downhole measurements the performance of the method has to be evaluated in relation to temperature conditions. SWD by drillbit source provides RVSP with quality depending on drilling conditions, with S/N related to the quality of the pilot signal. However, recent variants using also seismic interferometry, downhole measurements in the same well or in other wells, and large arrays of receivers can be adopted to improve S/N.

DAS is an important tool providing at affordable cost and with 'easy' installation conditions large arrays of measurements, that can be used for active-source monitoring and also passive monitoring. Wavefield separation processing can be easily utilized to recover dual signals, polarity, and immediate wavefield separation. With respect to conventional geophones and wireline tools, DAS cannot provide 3-component. However, DAS has much less limitations in high-temperature wells. However, it is envisaged that this condition will require some evaluation/analysis for the response of the fibre in the hot environments.

3.6 Conclusions

This study has been performed in the framework of the GEMex project, and focused in particular on the SHSG Los Humeros caldera. Starting from detailed structural model obtained by surface active seismic, we show by synthetic examples that VSP can predict the bedrock basement below the well, in other words, estimate how much distance is required to reach the target below the drilled depth. The borehole seismic tool (VSP) is of paramount importance for the evaluation of the geophysical information at depth, with direct time-depth calibration of subsurface structures at the well. For this reason, in the absence of legacy borehole seismic data, SWD and DAS methods have been evaluated for VSP application in SHGS systems. Both these methods are more robust in relation to high temperature conditions than conventional wireline VSP, and may easily provide large 3D images at depth. Advantages, limitations and acquisition parameters have to be evaluated and adapted for the specific selected cases of real future applications.

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4 Potentially Harmful Elements (PHE) mobility assessment in soils of Superhot Hot Geothermal Systems

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4.1 PHE mobility and PHE geochemistry in geothermal areas

Studies on the mobility of potentially harmful elements (PHE, Potential Harmful Elements) in active geothermal environments are limited while there is a countless number of publications concerning the mining environments and, in particular, the "Sulphide Mine Tailings" deposits (SMT), essentially consisting of iron and manganese oxides. SMT alteration, triggered mainly by the sulphates oxidation, is the basis of the formation of the Acid Mine Drainage (AMD) deposits which have similar geochemical characteristics (mineralogy, pH, redox, etc.) of the geothermal surface alteration zones and are also characterized by the presence of oxy-idroxides and clays minerals. In sulphide deposits AMD formation is enhanced by the presence of water, excess of oxygen and, sometimes, by the presence of bacteria species such as *Thiobacillus sp*. The oxidation of sulphides induces the formation of H₂SO₄ whose direct effect is the reduction of the pH values which cause an increase of the solubility and mobility of the metals (Benzaazoua et al., 2004).

According to Vidal et al., (2018), the geothermal environments can be considered as a system which is constantly changing and where the secondary minerals are superimposed as alteration products. In regions where the geothermal activity is strong and long-lasting, alteration produces pyrite, amorphous silica, anatase and native sulphur that are the main components of the soil superficial crust. On the other hand, when the geothermal activity is reduced, the main minerals will be kaolinite, Fe-oxides and oxihydroxides. These findings have been reported by Markússon and Stefánsson (2011) in a study regarding the surface geothermal alteration of a basalt in Iceland, where, in relation to the intensity of the geothermal activity at the surface, three weathering areas were described:

- I. high activity areas, with active steam vents and mud pots characterized by an intensive acid leaching;
- II. medium activity areas, where the ground is hot, steam vents and mud pots are uncommon and the surface alteration is less intensive;
- III. low activity areas, on the margins of the surface geothermal activity.

A schematic representation of these findings is shown in figures 4-1 and 4-2. It can be noticed that to each sector, with a different level of alteration, will correspond a neo formation mineral group association or a specific mineral both in the amorphous and/or crystalline state according to the chemical-physical conditions, emission flow intensity and temperature.

A consequence of the chemical-physical transformations is the total and/or partial breakage of the chemical bonds between the metals and the minerals to which they were previously associated. Breakage causes the release of metals into the environment and makes them available to participate in a new biogeochemical cycle. The primary factors influencing the steam-heated acid sulphate alteration of the geothermal deposits are the redox state of the "system" (oxidation front extension), the acidic supply, the pH value of the medium, and the extent of reactions (Figure 4-1).



Figure 4-1: Schematic geochemical model for the acid sulphate chemical alteration and related mineralogy in a geothermal environment. (Modified from Markússon and Stefánsson, 2001).



Figure 4-2: Simplified representation of the main mineralogical phase's distribution in a geothermal environment. (Modified from Markússon and Stefánsson, 2001).

It is evident that the formation of minerals containing iron and sulphur and their respective elemental mobility depend on the redox conditions. Pyrite formation is fostered in reducing conditions while goethite and/or hematite prevail in oxidizing conditions. At low pH, Ca, Mg, K and Na ions are mobile and leach out from the system, whereas elements, such as Fe, Ti, Al and, with a large degree, Si are

retained in the alteration products. At higher pH the mobility of Ca, Mg, K and Na ions is lower due to the clay's formation.

For these reasons the results of the AMD studies may provide useful suggestions about the investigation on the mobility of the elements in geothermal environment because redox reactions can mobilize (or not) metals in relation to the characteristics of the metal species. Moreover, sulphide oxidation is one the main process that promotes the system acidification and, then, the resulting metals release (Figure 4-1). In areas where sulphide mineralization occurs, pyrite is the most abundant mineral and the oxidation is usually followed by secondary minerals formation as Fe (III), Al and Mn hydroxides. Though these minerals are the major phases in the secondary mineral assemblage, they account for a low percentage in the bulk samples as observed in mine tailings or waste dumps. As a consequence, the identification and assessing of these minerals are quite difficult and it is therefore necessary to apply techniques or specific procedures able to discriminate among the metals bound to the different mineralogical phases.

The acid–sulphate alteration of active and fossil geothermal systems has been described in several studies: Klammer, 1997; Mas et al., 2006; Boyce et al., 2007; Karakaya et al., 2007. All authors proved that the water aquifer chemistry is controlled by geothermal fluids and associated minerals. Smectites and zeolites are the main minerals at low temperatures while, at higher temperature, they are replaced by actinolite, chlorite and epidote. Alkali-feldspar, sulphides, quartz and calcite result to be independent from temperature.

According to Heald et al.1987, water-rock interaction between steam-heated acid sulphate waters and primary rocks, typically produces alteration assemblages characterized by silicic and extended argillic alteration.

For these considerations, in a complex environment such as geothermal, the effect of weathering on the mineralogical and clay formation is to promote/foster "different" elements mobilization (enrichment or leaching) in relation to the local phase solution conditions: dissolution or formation.

Geothermal deposits are characterized by very low pH, and silicate and carbonate mineral associations are able to neutralize free protons produced by the sulphide oxidation and by secondary phase hydrolysis. Some authors have also suggested to utilize standard statistic methods to calculate the exact percentage of carbonate which has to be added to the system in order to buffer the acidity produced by the sulphide oxidation (White et al., 1999).

It is known that carbonate distribution in soil greatly influence the soil natural buffering potential. However, laboratory results on acid tailings mixed with limestone have shown that an excess of carbonate may reduce the rate of sulphide oxidation owing to the coating action of the secondary ferric phases on sulphides. (Lapakko et al., 1997; Holmstrom et al., 1999).

On the other hand, it has been also found that the carbonate (CO_3^{--}) excess could promote ions transfer via the surface of Fe (II)-CO₃ complexes fostering pyrite oxidation (Evangelou and Huang, 1994).

In geothermal districts, changes in environmental conditions may cause the variability of the fluid intensity emissions and, in relation to local tectonic and soil cracks or sealings occurrences, may determine modifications in vents distribution patterns. Besides, abrupt changes in soil gas emissions, temperature and redox potential, contribute to mobilization or/and re-mobilization of the heavy metals transported by fluids, inducing a potential risk for the environment and population.

The presence of the oxidation front and its thickness affect element mobility as evidenced by the occurrence of a transition zone from pyrite to hematite or/and goethite. This finding occurs especially if the acid-sulphate alteration succeeds at temperature close to 100°C. In these conditions, as expected, Ti is immobile while Fe, P and Si are leached out from the system. The silica mobility seems to be not related to the intensity of the geothermal activity.

The geothermal surface areas can be considered as 'open systems' where steam and fluid mixing occur with non-thermal shallow waters which lead a different fluid-rock interaction. Some elements could be precipitated as secondary minerals while others could be leached out from the 'system' (Markússon and Stefánsson, 2011). Moreover, it has been observed that the relative mobility of some elements in geothermal waters at pH<2.5 is high and water dissolve them stoichiometrically with the exception of Ti, Zr and Cu. When pH is rising (from 2.5 to 4), mobility decreases significantly. Aluminium mobility decreases quickly as soon as the pH increases being related to the formation of kaolinite in areas characterized by pH values that can change from medium to low.

4.1.1 Climate influence on element mobility

Climate affects the elements mobility in soil. In fact, in environments where moisture conditions prevail, the sulphide oxidation and the neutralization reactions release elements that are transferred downwards. On the other hand, where reducing conditions occur, elements are retained due to both secondary mineral precipitation and/or adsorption processes, depending on the pH values.

In dry environments, where oxidizing condition prevail as, for example, in Mexico geothermal areas object of study in GEMex Project, elements move preferentially upward via capillary forces and are transported and displaced towards the top soil horizons (Dold and Fontbote, 2001). These environments are also characterized by soils with low pH (<3-4) and, in the soil oxidation zone, by the easily formation of water-soluble sulphate. This finding has been also observed in the surface of copper mining tailings as reported previously. When tailings are characterized by high levels of carbonates, pH increases and metals mobility is strongly reduced because, in dry conditions, sorption processes predominate. In this situation, sulphide replacement process is a less important process and the precipitation of water-soluble secondary sulphates is controlled by the condition of soil saturation. For all these reasons, in geothermal areas characterized by arid climates regions, it is important to get information on the water-soluble fraction and it is necessary to start the soil extraction using a procedure that involves the use of an extracting solution able to dissolve secondary minerals and salts. (Blowes et al., 1998; Dold and Fontboté, 2002; Dold, 2003).

4.1.2 SEP, Sequential Extraction Procedures and PHE mobility

Selective dissolutions are useful techniques to study minerals phases that could be responsible for metal scavenging pathways as for Fe and Mn oxy-hydroxides in geothermal environment.

Sequential Extraction Procedures (SEP) represent a practical and useful tool to study metal mobility, representing a suitable approach to understand metals speciation in relation to a specific extractant and extraction procedure adopted (operationally defined).

Trace element distribution in soils depends on several parameters and, in particular, on the solid phase composition. This means that an element is preferentially associated to a specific soil component and will be released as a consequence of chemical or physical changes. In fact, changes in environmental conditions as redox potential and pH, can induce, together with organic matter degradation, the release of the heavy metals in the "system" and, as a consequence, the increase of their mobility. To reduce this

risk, it is important to identify the binding sites and the mineralogical phases that are involved in order to evaluate a possible metal remobilization.

Abrupt environmental changes can also damage soil microorganisms increasing the risk of possible contamination. In fact, the presence of microorganisms reduces metal redox charge, as it has been observed for Hg and U that are among the most studied elements in this environment. It has been also observed that detoxification contributes towards a lower metal mobility reducing the potential toxicity.

Therefore, speciation studies, based on sequential extraction procedures are carried out using extractants able to selectively complex chemical species that are linked to specific soil components, simulating both natural geochemical processes and changes due to anthropic actions. (Gupta et al., 1996; Fanguero et al., 2002). As a general consideration, the difficulty in this field of research is represented by the remarkable number of methods proposed, by their lack of uniformity and by the complex and time-consuming procedures involved. In addition, frequently a problem is represented by the lack of selectivity of the extracting solutions used. Selectivity can be increased adapting the sequential extraction method to the mineralogy and checking the dissolved mineralogical phase by X-ray analysis after every leaching test. However, full selectivity can't be achieved because the considered mineral species may not dissolve completely while, at the same time, other minerals, instead of being stable, could be partially leached.

Notwithstanding all the criticisms these procedures are the main tool that we can apply to evaluate PHE mobility and their behaviour in soils.

In geochemistry, trace element speciation in soils is usually assessed performing sequential extractions of the solid matrix. Mostly speciation schemes rely on the use of one or more steps of separation, followed by element-specific detection (Bermond et al., 1998, 2005). One of the best-known sequential extraction schemes was elaborated by Tessier et al. (1979). This procedure consists of five steps in which heavy metals are extracted in different phases.

Many single or sequential extraction procedures, mainly based on Tessier procedure or on its different modified versions, have been applied to soils and sediments to fractionate metals by using different extractants to obtain detailed information about the bioavailability and mobility of the metals. Metal fractionation depends on the nature of the extractant used and on the operating conditions of the extraction procedure. (Fanguero et al., 2002; Labanowsky et al., 2008).

Many studies report that, through each leaching test, some minerals can be partially or totally destroyed so, for a complete geochemical interpretation, a mineralogical study of each residual phase should be also considered.

With the aim of harmonizing the different elaborated methodologies throughout the European Union, and improving the comparability between obtained results, the Community Bureau of Reference Materials (BCR) developed a simple, three-stage sequential extraction protocol operationally defined for the speciation or fractionation of trace metals in soil and sediment samples. The BCR sequential extraction procedure has been widely applied to soil and sediment samples as a standard reference procedure (Pueyo et al., 2003).

It is not easy to choose between two extractions protocols (single or sequential) the approach most appropriate to assess the chemical form to which metals are bound to soil. Single or sequential extraction procedures are carried out under equilibrium conditions and, as a consequence, may have limited applications. For this reason, many authors have suggested to adopt the kinetic extraction protocol utilizing a single extractant (Fangueiro et al., 2002). Two procedures, that can't be easily compared in terms of experimental performances, are usually performed in kinetics studies. One of these consists of a single extracting solution generally used in a soil/solution ratio of 1 to 5 with the sample solution kept under stirring and collected at different (increasing) times.

The other procedure operates using several extracting solutions with different molarity and pH values (such as, EDTA, DTPA, Acetic Acid, etc) and considers different sample stirring times for each extraction step.

A summary of the most utilized single extracting procedures for soils that can be also applied for geothermal soils, with the corresponding extracting solution, are reported in table 4.1.

Phase/Fraction	Extracted phase	Most common extractant
Water soluble	Most mobile soluble metals including free ions and ions complexed by the soil organic matter. Techniques as filtration and ultrafiltration are utilized to separate this phase. Centrifugation is another common employed technique.	Deionized water Hot water
Exchangeable	Metals weakly adsorbed to soil by electric charges and mobilized by ion exchange processes. This fraction represents 2-3% of the total available metals.	0.43 M Acetic acid 1 M Ammonium chloride 0.01–0.5 M Calciumchloride 1 M Potassiumchloride 0.2 M Potassium nitrate 0.1 M Sodium nitrate
Specifically sorbed	This phase includes the less readily exchangeable elements that are specifically sorbed by covalent forces.	0.5 M Acetic acid 1 M Ammonium acetate or 1 M NH_4NO_3 at pH 6
Bound to Organic Matter (O.M.)	This phase consists of metals associated to living organisms or their decomposition remains. Decomposition enhances soluble elements release under oxidizing conditions. This fraction is also associated to low mobility high molecular weight humic substances. Organic mineral and amorphous phase display different degree of selectivity and binding capacity to complex metal ions.	0.1M Na or K-pyrophosphate 0.1/0.7 M Na-hypochlorite 0.4 M EDTA H ₂ O ₂ /HNO ₃ /Na-Acetate
Bound to Carbonate	This phase preferentially adsorbs free ions in environments with low O.M. or/and Fe-Mn oxides contents. Phase sensitive to environmental changes as acidification that leads to the solubilization and mobilization of metals.	0.1; 0.2;0.5M Acetic acid 1 M Sodium acetate/Acetic acid at pH 5. 0.05 M EDTA
Bound to Mn and Fe oxides	Fe-Mn hydrous oxides are scavengers of heavy metals. Their formation is related to main factors as precipitation, adsorption, surface mineral coatings, ion exchange, etc.	0.1M Hydroxylaminehydrochloride Dithionite/citrate/bicarbonatepH 7.3 0.1MHydroxylamine hydrochloride 0.1 M Oxalate
Pseudo-total and bound to silicate Residual	From environmental studies pseudo-total extraction, utilizing HNO ₃ , HCl or Aqua Regia, well represents the maximum level of the extractable metals. Many EC countries employ Aqua Regia extraction as legal procedure to certify extractable trace elements in soils.	HNO₃, HCl, Aqua Regia (Pseudo-total)
	Complete silicate dissolution can be achieved only introducing in the last dissolution step strong acids as HF and/or HClO ₄ .	Mix of HNO₃-HF-HClO₄ (Total)

Table 4.1: Single extracting procedure: description of the extracted phase and of the most utilized extracting solutions according to literature.

The most utilized geochemical approaches for the evaluation of metal mobility in soils can be summarized in the following scheme:



The extractants described in this table 4.1 are utilized preferentially to focus a given phase. Besides, by combining different extractants in a sequential extraction scheme, their specificity can be enhanced.

In geothermal areas, where soil temperature can change (more than 100°C with depth and sideways) and vertical or lateral non-homogeneous soil conditions can occur, sampling campaign should consider first of all the historical and geological conditions of the site. Sampling plan should have a statistical sampling approach which allows to distinguish between the natural background trace elements pattern from the possible effects of geothermal exploitation which could produce a heterogeneous distribution of trace elements. Moreover, sample storage and pre-treatments should be performed utilizing appropriate tools to avoid cross contamination and to obtain representative samples.

Some practical advices related to samples collection and pre-treatments to be easily applied also to geothermal soils, are summarized in Table 4.2.

	Collection	Pretreatment					
Sampling	 Site historical information Consider lateral and vertical homogeneity of the geothermal soil Geology, morphology, tectonic pattern, etc. Vegetation distribution. 	 Preserve original sample characteristics. Select appropriate dry temperature to avoid loss of volatile elements (e.g. Hg, As, Se), reduce oxide formation and microbiological activity. Utilize working dry temperature from 30 to 40°C. Freeze drying warranty repeatable results Utilize <2mm nylon sieve to avoid contamination. Perform sample homogenization by hands or using mechanic tools. Perform acidification of the samples and utilize cold storage environment to maintain the stability of the soil extracted solution. 					

 Table 4.2: Description of "good practices" for soil sampling procedures in geothermal environment.

Sample pre-treatment should not disturb the original physical and chemical conditions of the sample. Sample storage should be limited as much as possible the onset of changes in the characteristics of the sample and avoid both the action of microorganisms and chemical transformations.

For this reason, the question to preserve the samples with their moisture content or to dry them at temperatures that can minimize any change in the chemical-physical state, such as oxidation and / or reduction, is debated. This is to prevent the loss of some elements and, in particular, the volatiles such as Hg, As, and Se.

Studies regarding the problematic of the homogeneity and the representativeness of the sample have shown that the weight limit of 100g of sample to be treated originally represents a good compromise, considering that also reference materials have been prepared for the same use with reduced weights, in order to increase the sample homogeneity and the measurements reproducibility.

In the field of Sequential Extractions it is a common practice to employ dried samples that remain stable for a long time (1-2 years). Draying temperature is usually kept below 40°C to avoid, among other things, the release of the more volatile elements. In this regard it is recalled that in many natural

situations soils are exposed for long time to strong sun radiation and surface temperatures easily exceed this limit value that, for these considerations, is now widely used. However, some authors pointed out that it would be advisable to keep the temperature below 30°C as samples dried at 40 °C and stored for more than one year, showed an increase in extractability, only for Cu and Cr, while for other heavy metals extractability remains unchanged. (Rao et al., 2008, Rauret et al. 2000).

Finally, one aspect to consider is the sample manual re-mixing after each extraction in order to avoid the separation of the soil particles in the extracting bag since the metal extractability depends on the size and spatial distribution of the particles.

Concerning the extracted solution, acidification is strongly recommended because this procedure increases ion stability and the storage time.

4.2 Potentially Harmful Elements (PHE) mobility assessment in geothermal soils: comparison between two cases studies from Los Humeros (Mexico) and the Phlegraean Fields (Italy).

4.2.1 Introduction

The geothermal resources are mainly present in environmentally sensitive areas therefore, exploration and exploitation should be carried out following procedures and practices capable of minimizing any environmental negative impacts in order to preserve wildlife habitats, vegetation and local communities. On the other hand, geothermal areas are characterised by high levels of Potentially Harmful Elements (PHE), particularly of some heavy metals such as As, Cd, Cu, Pb, V, Zn and Hg that, in specific circumstances, show higher mobility. These elements are present in fumarolic gases and in depositional products as sublimates and condensates. In such areas trace element mobility is promoted by the low pH and by the complex chemical reactions fostered by the soil high temperature and by selected microorganisms adapted to survive in these extreme conditions.

International literature on this topic has stressed, as an example, the high concentration levels of As and Hg in volcanic soils and in related geothermal waters. Besides, the toxic arsine gas (AsH₃) has been found in some Italian fumarolic gases emitted from Vulcano island soils (Signorelli, 1997; Bundschuh and Prakash Maity, 2015 and reference herein; Wang et al., 2018).

Owing to these difficulties, suitable tools to display PHE distribution patterns and concentration levels in geothermal areas are necessary in spite to manage actions to reduce both the potential pollution effects and the risk for the population.

Volcanic gases and fluids have large variability in composition (both in element and compound contents) for several factors as:

- i. different time period sampling collection;
- ii. differences among fumaroles vents even if they are in the same geothermic area;
- iii. influence of meteorological conditions since rainwater acts as a diluting factor.

Last but not the least, a problem arises when we compare data obtained by different sampling and analytical methods.

One of the main environmental concerns associated with the geothermal plants is related to the discharge of large volumes of hydrogen sulphide and carbon dioxide. Gases include hydrogen, methane, nitrogen and oxygen, Hg, As and other heavy metals. For shallow aquifers pollution impacts can change with the aquifer usages, percolation rate and relationship between the aquifer and the other surrounding waters.

Nowadays fast analytical data are requested to help decision makers and/or to provide information in defining sampling activities. For these reasons is necessary to develop simple techniques and procedures for the screening of a great number of samples. To be advantageous, screening procedures should be characterized both by on site monitoring low cost and by the possibility of giving rapid responses in spite of collecting representative samples that will be successively analysed by conventional laboratory methods. Furthermore, problems related to the storage and transport of the samples should be reduced with significant advantage of reducing the time and the cost of the analyses. This procedure should also involve little or no sample treatment differently by those utilized for conventional analytical processes. It is important to minimize sample treatments since the sample treatment is time-consuming, expensive,

it can represent a source for major random and systematic errors and require the use of chemicals capable of being dangerous for operators and the environment. The semi quantitative response provides reliable indication which can be used for immediate decision-making. As regards the assessment of remediation studies in soil contaminated by heavy metals, this approach is particularly useful in order to plan a successful sampling strategy.

Although most of the environmental directives set strict limits on the levels of the total concentrations of potentially toxic elements, in recent years many studies have demonstrated that the total metal content levels in soils are not enough to assess a potential environmental risk due to metals. More suitable information can be obtained evaluating the environmental mobility and bioavailability of some potentially toxic elements as those selected for this study considering the step-by-step fractionation, operating with different reagents or extractants together with extraction procedures, operationally defined, with the purpose of evaluating the environmental available metal fraction (Ure A. M., 1993; Mester Z., 1998).

In the framework of GEMex project, WP 8.4, we propose a study whose aim is to test an extraction procedure on geothermal soils to suggest a suitable and wide-ranging procedure that can be easily utilized and adapted to the peculiar characteristics of these environments. In this way might be possible to relate metal mobility to the associated minerals phases. Chemical associations have been studied comparing total soil content with the metals extracted concentrations in the different steps of a sequential extraction step procedure that reasonably permits to assess the potential hazard of metals.

GEMex project aims to achieve objectives of general significance capable of being applied in geothermal areas of all over the world, in this view, we compared the results of metal mobility study obtained from some Mexican geothermal soils (Los Humeros) with data obtained investigating metal availability on soils collected in the Phlegraean Fields, Naples, Italy.

4.2.2 Sampling and analytical methods

4.2.2.1 Sampling and soils treatment

Top soil samples (0-5 cm) were collected in two geothermal areas in Mexico and Italy (Figures 4-3 and 4-4) with the aim of characterizing those soils subjected to the action of hot hydrothermal fluids and comparing them with soils, with similar characteristics, located in the same geothermal context, but in "cold" conditions due to the absence of the influence of the hydrothermal fluids.

Soils from Mexico were sampled in two sites from Los Humeros geothermal area (Loma Blanca and Xalapazco Crater) by the colleagues involved in the activities of the WP5 GEMex project. The geochemical comparison was performed on soils sampled in the Phlegraean Fields geothermal area, (Naples, Italy) by the GEMex Enea team that organized a dedicated sampling survey (Figures 4.3 and 4.4).



Figure 4-3: Soil samples location in Los Humeros, Mexico. LB: Loma Blanca; XA: Xalapazco Crater



Figure 4-4: Soil sample location in the Phlegraean Fields, Italy



Figure 4-5: USDA Textural classification diagram for Phlegraean Fields (CFP) and Los Humeros (LB, XA) soils.

4.2.2.2 Particle size analysis, pedological and geochemical soil properties

Soil samples location has been reported in Table 4.3 for soils collected in Mexico, at Loma Blanca, a site that is close to the Los Humeros geothermal power plant and for the samples collected in the Phlegraean Fields, in Italy. After the sampling campaign, in laboratory soil moisture has been removed drying samples in a thermostatically controlled oven at 40°C.

Grain size analysis has been carried out weighting exactly 50 g of soil which was soaked in a solution of distilled water and sodium hexametaphosphate at 0.05% Vol, to permit the dispersion and prevent fine particles flocculation. In order to remove the organic substance, H_2O_2 was also added. Samples were sieved wet using a 50 μ m mesh sieve. The supernatant fraction was then dried again, sieved and the various aliquots weighed, while the remaining fraction examined by a sedigraph (Sedigraph 5100 from Micromeritics). The "skeleton" containing the particles with a diameter greater than 2 mm (gravel) was cut apart from the "fine earth", characterized by particles with diameters less than 2 mm (sand, silt and clay).

According to the USDA classification method (U.S.D.A, United States Department of Agriculture, Soil Taxonomy, 1999) the grain size percentages of the fine particles (Sand, Lime, Clay) permit us to classify the soils utilizing triangular diagrams that have been reported in Figure 4-5.

The textural analysis shows a certain homogeneity between the Loma Blanca and Phlegraean samples. In fact, they fall into the contiguous fields of the Loamy Sand and Sandy Loam. The only exception is sample XA1 in which the fine fraction is prevalent.

From a geochemical point of view the textural affinity highlighted between soils coming from different geothermal regions could suggest a certain similarity in the complexation capacity of heavy metals by soil particles. It is known that, as the particles size decreases, the volume of the adsorption surface increases and the complexation capacity of the adsorbed free ions increase.

Soil pH measurements were performed using a portable 250A Orion pH Instrument (Thermo Electronic corp.) equipped with an Orion gel-filled combination pH-electrode (Thermo Electronic corp.).

The studied soils were sampled selecting carefully areas with different geothermic properties; the first typology of selected site is characterized by an evident geothermal activity, the other by the absence of activity. Consequently, a considerable difference in soil temperatures was observed as shown in table 4.4. However, soil temperatures in the most active areas fall within a close range: in fact, soil temperature in Loma Blanca was 64 °C (sample LB1) and 93°C (sampleXA1), while the Phlegraean Fields soils account for a surface temperature in a range from about 70 to 114 °C.

Concerning the areas characterized by an evident lack of geothermal activity and, therefore, to be considered 'cold', two sites have been identified in Loma Blanca (soils LB2 and XA2) typified, respectively, by temperatures of 20.5 and 22 °C. The two cold samples from the Phlegraean Fields, with a surface temperature of 9.4 and 9.7 °C, respectively, were samples CFP5 and CFP7 (Table 4.4).

In this regard, it should be remembered that geothermal fluids temperatures and emissions are generally extremely variables depending on several local parameters including meteorology and precipitation intensity and frequency. Thus, the temperature can differ, over time, within a wide range. Considering that the purpose of this activity within the Gemex project is to study the mobility of some metals in a geothermal environment, these temperatures can be considered sufficiently representative for this type of worldwide situation.

The total concentrations of the metals determined in the two set of the investigated soil, expressed as mg/kg, have been reported in Table 4.4.

	Sample	Т°С	рН
Phlegraean Fields, Italy			
33T 428045E 4520106N	CFP1	70.2	3.23
33T 428041E 4520103N	CFP2	75.5	3.39
33T 428106E 4520102N	CFP3	113.6	3.30
33T 428089E 4520136N	CFP4	101.0	1.51
33T 428135E 4520192N	CFP5	9.4	6.08
33T 428034E 4519727N	CFP6	94.7	4.10
33T428575E 4519629N	CFP7	9.7	7.10
Los Humeros, Mexico			
14Q 661868E 2177309N	LB1	92.6	1.52
14Q 661838E2177302N	LB2	11.3	3.71
14Q 663488E 2172561N	XA1	64.5	1.18
14Q 663470E 2172665N	XA2	12.5	3.69

Table 4.3: Samples location, T°C and pH for the geothermal soils from Los Humeros, Mexico and Phlegraean Fields, Italy.

Sample	As	Cd	Cr	Со	Cu	Fe	Mn	Ni	Pb	V	Zn	Hg	U
Phlegraean Fields													
CFP1	11.6	.114	7.08	1.15	7.84	11708	37.6	1.55	112	78.8	19.2	2.10	6.36
CFP2	17.3	.317	11.3	3.05	16.7	21988	294	2.44	75.3	77.0	43.8	3.80	8.34
CFP3	18.1	.274	7.26	0.87	11.3	26919	312	1.52	77.2	61.3	22.2	0.87	4.50
CFP4	2.07	.257	2.11	0.34	1.11	837	16.0	3.00	23.5	18.7	5.20	89.0	9.00
CFP5	8.80	.206	8.60	2.47	13.5	11788	252	2.60	46.4	44.0	114	1.80	4.65
CFP6	22.0	.334	18.0	7.12	102	24095	972	1.68	112	99.4	148	0.57	6.26
CFP7	19.4	.260	3.47	5.95	14.6	22800	750	1.33	53.5	76.0	101	0.03	5.81
Los Humeros													
LB1	0.700	.282	9.62	0.44	2.04	2363	41.0	<loq< td=""><td>10.8</td><td>20.3</td><td>15.4</td><td>4.00</td><td>1.51</td></loq<>	10.8	20.3	15.4	4.00	1.51
LB2	2.76	.180	44.0	0.98	5.43	14458	17.4	1.20	21.5	65.3	12.4	0.41	1.75
XA1	0.327	.077	223	0.53	4.42	2742	3.80	2.01	10.8	179	1.21	39.0	0.90
XA2	0.600	.132	120	23.2	29.6	39207	524	63.1	10.5	74.4	65.2	1.90	1.88

LOQ for Ni = 1.00 mg/kg

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Table 4.4: Trace elements total contents in Los Humeros and Phlegraean Fields geothermal soils (mg/kg).

Table 4.4 and Figure 4-7 account also for soils pH values. Although the number of samples cannot be considered relevant for a statistical elaboration, it is clear that the lower pH values correspond to soils at higher temperatures. The "cold" soils, at least in the Phlegraean Fields, show pH values close to neutrality and quite similar to the values considered typical for the world soils which, commonly, are characterized by pH values comprise in the range from 6.5 to 8.

Considering the importance showed by soil pH values in influencing the mobility of the metal elements, these data could be very useful for the discussion and for the final data analysis. (Daskalopoulou et al., 2014). Although already existing a large bibliography on the distribution of trace elements in soils, publications concerning the geothermal areas are rather limited, probably because of the particularity of these environments.

On the other hand, more data are available for volcanic soils which, among all geological environments, are those with the geochemical characteristics more comparable to the geothermal areas. These, from a geochemical point of view, could be considered as "anomaly areas" owing to the high levels of many trace elements that are associated to residual magmatic fluids. Therefore, they are excluded from minerals or complex formation and are easily released directly into the atmosphere and on the soil surface as gases or fluids. For this reason, geothermal soils are characterized by anomalous levels of PHE respect those considered typical for other environments of the earth's crust, as reported in Table 4.6 where, for some elements, it was also possible to report the concentration value considered excessive for a 'natural' soil and what could probably be considered typical before the industrialization and the impact of anthropogenic activity.

Moreover, the very low values of pH of the geothermal soils, together with the high soil temperature, represent an aspect that could enable metal ions mobility. In fact, in these particular chemical-physical conditions mobility can be enhanced and metal elements can easily enter the biogeochemical cycle.

Table 4.6 reports a summary of some PHE concentration levels in soils derived from volcanic rocks. The lack of information for some elements is an evidence of the difficulty to find data even for some elements that are considered important from an environmental and toxicological point of view.

However, with the limited available data found it was possible to fill table 4.7 that reports the Hg levels in top soils from some geothermal areas worldwide. Here Hg exhibits a concentration range from 0.010 to 1.9 mg/kg. Since the average levels calculated for natural soils vary from 0.050 to 0.1 mg/kg, it is evident that the highest concentrations of Hg in geothermal areas can exceed about 20 times these values.



Figure 4-6: Soil temperatures distribution pattern inside the Solfatara crater, Phlegraean Fields Area, Naples, Italy. Enea unpublished data from a 2002-2015 survey.



Figure 4-7: Variation of the soil pH in Phlegraean Fields (CFP) Italy and in Los Humeros, (LB and XA) Mexico.

Milestones	As	Cd	Со	Cr	Cu	Hg	Ni	Pb	Sb	Zn	Reference
UCC*	2.0	0.10	11.6	35	14.3	0.056	18.6	17	0.31	52	Wedepohl,1995
UCC*	4.8	0.09	17.3	92	28	0.050	47	17	0.40	67	Rudnick & Gao, 2003
World soils		0.10		61	23		27	26		74	Li, 2000
European soils		0.79		53	19.5		27	39		68	Angelone & Bini, 1992
World soils		0.30		200	20		40	10		50	Angelone & Bini, 1992
World soils	4.7	1.10	6.9	42	14	0.10	18	25	0.62	62	Kabata-Pendias & Mukherjee, 2007
World soils	6.0	0.35	8.0	70	30	0.06	50	35		90	Adriano, 2001
Excessive levels in soils		5.00		100	100		100	200		250	Kabata-Pendias, 2000
Pre industrial levels in soils		0.55		48	34		40	22			Callender, 2003

*UCC, Upper Continental Crust

Table 4.5: Reference levels of some PHEs in world rocks and soils (mg/kg).

Parent material	As	Со	Cr	Cu	Hg	Ni	Pb
Rhyolites, Trachytes, Dacites			30-116 (78.5)				
Volcanic Rocks USA	2.1-11.0 (5.9)	5-50 (17)		10-150 (41)	0.01-0.18		10-70 (20)
Various soils from Basalts and Andesites						4-370	
Various soils from Serpentine rocks suite						770-7000	

Table 4.6: Concentration levels for some trace elements in volcanic soils. Kabata-Pendias 2000, 2007. Values in brackets are the mean.

Location	mg/kg	Reference	
Mercury			
Long Valley (California, USA)	0.100-1.90	Klusman and Landres, 1978	
Puna, Haway islands	0.015-1.13	Cox, 1981	
Sulawesi, Indonesia	0.040-0.30	Suryantini, 2013	
Tuscany	0.020-0.30	Baldi, 1988	
Mexicali, Mexico	0.010-0.26	Pastrana-Corral et al.,2016	
Arsenic			
Tibet, Cina	1.80-155 (mean 19)	Sheng et al., 2012	
Kuala Selangor, Malaysia	up to 2478	Ashraf et al., 2011	
Vinto, Bolivia. Geothermal smelter area	825-3390	Rotting et al., 2014	

Table 4.7: Mercury and Arsenic levels in top soils from some geothermal areas.

4.3 Chemical characterization of the soils: total trace element determinations

Total content of the trace elements in the soil samples were determined performing a microwave-assisted acid digestion according to a procedure described below:

0.25-0.30 g of soil sample were carefully weighed directly in the Teflon vessels of the microwave digestion system and the following mixture of reagents was gradually added to all samples in this sequence:

- 9 mL of 69% HNO₃;
- 2 mL of 30% H₂O₂ (in aliquots of 0.5 mL);
- 3 mL of 40% HF.

After a first dissolution carried out at room temperature, the samples were placed in the microwave system to proceed with their dissolution at high pressure and temperature. Once cooled, the obtained solutions were evaporated using the proper evaporation module of the microwave instrument with the aim of eliminating the excess of hydrofluoric acid, in order to avoid possible damage to the quartz instrumentation used in the subsequent analytical determinations. At the end of the evaporation process the residues once achieved a rubbery consistency, were quantitatively transferred to a 50 mL volumetric flask, acidified with 1% HNO₃ and diluted to the final volume with H₂O MilliQ and, then, stored at 4 $^{\circ}$ C until the time of the analyses.

Adequate quality assurance for the determinations of the total metal concentrations in the studied soils was guaranteed by analysing, using the same procedure used for the soil samples, the Standard Reference Material 2711a Montana Soil. The results of the quality control analysis have been reported in Table 4.8.

	Montan	a Soil				
	This study	Ref. values				
	mg/kg					
As	113 ± 7	107 ± 5				
Cd	58.8 ± 4.5	54.1 ± 0.5				
Со	10.6 ± 1.0	9.89 ± 0.18				
Cr	49.8 ± 4.3	52.3 ± 2.9				
Cu	150 ± 9	140 ± 2				
Fe*	3.00 ± 0.40	2.82 ± 0.04				
Mn	708 ± 82	675 ± 18				
Ni	19.6 ± 3.4	21.7 ± 0.7				
Pb*	0.153 ± 0.02	0.140 ± 0.001				
U	2.63 ± 0.69	3.01 ± 0.12				
V	85.7 ± 3.5	80.7 ± 5.7				
Zn	427 ± 2	414 ± 11				

* Value as %

Table 4.8: Quality control results for Montana Soil 2711a, Standard Reference Material, utilized in this work.

The determination of the Hg total concentration in soils was performed by the Automatic solid/liquid Mercury Analyzer, AMA, directly on the dry sample and, to verify the reliability of the analytical procedure used, certified reference materials, MESS-4 e PACS-3, were analysed at the same operational conditions and at the same time of the soil samples. The obtained results, for each CRM, are shown in Table 4.9.

	ME	CSS-4	PACS	-3				
	mg/kg							
	This study	Ref. value	This study	Ref. value				
Hg	0.07±0.05	0.08±0.06	3.30±0.20	2.98±0.36				

Table 4.9: Quality control results for total Hg in CRMs MESS-4 and PACS-3.

Reagents

69% nitric acid (HNO₃), Aristar[®] (BDH); 40% fluoride acid (HF), Aristar[®] (BDH); 30% hydrogen peroxide (H₂O₂). Ultrapure water (18.2 MW cm at 25°C), obtained from a MilliQ Element system (Millipore), were used for the preparation and dilution of samples and calibrating solutions.

Procedural blanks, inclusive of all potential contamination sources (impurities of reagents and contamination from materials used for sample handling) were always evaluated.

Polypropylene Falcon Tubes (Blue Max TM) and bottles were used during sampling handling

Instrumentations

A microwave system (Ethos Easy, Milestone) was used for sample digestion.

All measurements of trace element concentrations were carried out using a 7800 ICP-MS Agilent in He mode.

For Hg total content measurements in soil samples, the Automatic solid/liquid Mercury Analyzer (AMA-254, FKV) was used.

Measurements

 $10 \ \mu$ g/mL internal standard solution of Bi, Ge, In, Li, Sc, Tb, Y (Agilent Technologies) and $1000 \ \mu$ g/mL multi-elements standard solution of Ca, Fe, K, Mg, Na, e $10 \ \mu$ g/mL di Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V, Zn (Agilent Technologies), were used for the analytical measurements, performed by 7800 Agilent ICP-MS.

4.3.1 Sequential Extraction Procedure SEP

The step-by-step methodological description of the preparation of the extracting solutions utilized for the BCR sequential extraction procedure, according to Rauret et al., 1999, is provided below.

Solution A: acetic acid $CH_3COOH(0.11 \text{ mol } L^{-1})$

12.5 mL of glacial acetic acid CH₃COOH were added to about 300 mL of demineralised water in a 500 mL volumetric flask and were made up to the final volume with H₂O MilliQ to have a solution of CH₃COOH 0.43 M. Subsequently, 64 mL of this solution were diluted with H₂O MilliQ, to a final volume of 250 mL in a volumetric flask to obtain the A solution of CH₃COOH with a concentration equal to 0.11 M. The A solution is then transferred into a polypropylene bottle and kept in the refrigerator at 4 ° C until analysis.

Solution B: hydroxylamine hydrochloride NH₂OH·HCl (0.5 mol L^{-1})

8.77 g of hydroxylamine hydrochloride NH2OH • HCl were weighed and dissolved in 100 mL of H_2O MilliQ. Then, the solution was transferred to a 250 mL flask by adding 6.25 mL of HNO3 2M previously prepared and making up to the final volume with H_2O MilliQ. The resulting concentration of the NH₂OH • HCl solution is 0.5 M. The solution B, transferred to a polypropylene bottle, was used immediately after its preparation for extraction.

Solution C: hydrogen peroxide H₂O₂ 30%

Hydrogen peroxide was used as supplied by the manufacturer.

Solution D: ammonium acetate CH_3COONH_4 (1.0 mol L^{-1})

38.54 g of ammonium acetate were weighed and dissolved in about 450 mL of H₂O MilliQ. The pH of this solution was adjusted to 2.0 ± 0.1 by subsequent additions of 69% HNO₃ nitric acid (15.2 M). Subsequently, the volume of the solution was made up to 500 mL checking the pH and the resulting solution was transferred to a polypropylene bottle.

Extraction Step*	Reactive / concentration / pH	Solid phase
1	Solution A : Acetic acid, CH₃COOH (0.11molL ⁻ 1), pH 2.85	Exchangeable and weakly adsorbed fraction
2	Solution B: Hydroxylammonium chloride, NH ₂ OH·HCl (0.5 mol L ⁻¹) at pH 2	Reducible fraction bound to: Fe and Mn oxides
3	Solution C: Hydrogen peroxide, H ₂ O ₂ (8.8 mol L ⁻¹), followed by Solution D: ammonium acetate: CH ₃ COONH ₄ (1.0 mol L ⁻¹) at pH 2	Oxidisable fraction (organically-bound and sulphide-bound substance and sulphides)
Residual	69% HNO ₃ + 40% HF + 30% H ₂ O ₂ (9:3:2)	Remaining, silicate bound metals

In Table 4.10 it is shown the schematic representation of the BCR extraction procedure

Table 4.10: Schematic representation of the BCR extraction procedure

Procedural blank:

With each batch of extractions, a blank sample (a bottle with only the extracting solutions) was carried through the complete procedure and analysed at the end of each extraction step.

Reagent blank:

A sample of each batch of A, B, C and D solutions was always analysed.

Analytical performance

Adequate quality assurance was guaranteed by performing, for each batch of sample extraction, the extraction of CRM BCR 701 using the same sequential extraction procedure used for the soil samples.

4.3.2 Description of the three step of the extraction procedure

Step A: exchangeable and carbonate fraction

20 mL of the A solution (CH₃COOH 0.11 mol L⁻¹) were added to aliquots of about 0.5 g of the soil sample, carefully weighed in polypropylene tubes. The mixtures were shaken for 16 hours, at room temperature on/by an end over-end shaker at a speed of 30 rpm. Subsequently, the extracts were separated from the solid residue by centrifugation at 4000 rpm for 20 minutes and stored in test tubes at 4 ° C until analysis. The residue was then washed with 10 mL of H₂O MilliQ with an end-over-end shaker for 15 minutes. Then it was centrifuged at 4000 rpm for 20 minutes to remove the supernatant. The residue thus obtained was subjected to the subsequent extraction step.

Each sample was extracted in triplicate and a blank test (procedure blank) was carried out for each extraction step.

Step B: easily reducible fraction

20 mL of NH₂OH-HCl (0.5 molL⁻¹) were added to the residue from step A. The extraction procedure was then carried out as described in step A. After washing the solid residue with H₂O MilliQ, it was ready for the third extraction step (step C).

Step C: oxidizable fraction

5 ml of H_2O_2 (8.8 mol L⁻¹) were carefully added in small (0.5 mL) aliquots to the residue, obtained from step B. The tubes containing the solutions were covered, left at room temperature for 1 h and shaken occasionally, in order to allow a first digestion of the residue. Digestion continued for 1 h by placing the tubes with the solutions in a water bath set at 85 ° C; after 1 h, the tubes were opened to reduce the volume of the solutions to less than 1.5 mL. A further aliquot of 5 mL of H_2O_2 was then added to the residue by repeating the procedure described to obtain a final volume of the solutions less than 0.5 mL, avoiding to dry the solutions.

Once cooled, the residues were extracted with 25 mL of CH_3COONH_4 (solution D). The extraction procedure was analogous to that described in step A.

Acid dissolution procedure for total metal content determination in the residues from SEP

The total content of trace elements in the solid residues, obtained from step 3 of the BCR sequential extraction of the soils, were determined performing a microwave-assisted acid digestion.

The procedure is the same followed for the determination of the total metal content in the soil samples. Residue obtained at the end of the third extraction was carefully and quantitatively transferred to a suitable digestion vessel with about 3 mL of MilliQ water then, the following mixture of reagents was gradually added in this sequence:

- 9 mL of 69% HNO₃;

- 2 mL of 30% H₂O₂ (in aliquots of 0.5 mL);
- 3 mL of 40% HF.

After a first dissolution carried out at room temperature, the residues were placed in the microwave system to proceed with their dissolution at high pressure and temperature. Once cooled, the obtained solutions were evaporated using the proper evaporation module of the microwave instrument for the elimination of the excess of hydrofluoric acid, which may damage the quartz instrumentation used for the analysis. At the end of the evaporation process, the residues were transferred to a 50 mL volumetric flask, acidified with 1% HNO₃ and diluted to the final volume with H₂O MilliQ and, then, stored at 4 $^{\circ}$ C until the time of the analyses.

Reagents and apparatus

69% nitric acid (HNO₃), Aristar[®] (BDH); 40% fluoride acid (HF), Aristar[®] (BDH); 30% hydrogen peroxide (H₂O₂), AnalaR (NORMAPUR); 99% glacial acetic acid (CH₃COOH), (RUDI PONT); 99% hydroxylamine hydrochloride (NH₂OH·HCl), (FLUKA); ammonium acetate (CH₃COONH₄), (RUDI PONT). Ultrapure water (18.2 MW cm at 25°C), obtained from a MilliQ Element system (Millipore), were used for the preparation and dilution of samples and calibrating solutions.

All laboratory glassware was soaked in 4M nitric acid overnight and, then, was repeatedly rinsed with ultrapure water before use, to eliminate any contamination.

Polypropylene Falcon Tubes (Blue Max TM) and bottles were used during sampling handling.

Instrumentations

The extractions were performed using an end-over-end shaker Rotator Drive STR 4 (Stuart Scientific) at a speed of 30 rpm; the separation of the extracts from the residue was obtained by centrifugation using an ALC Centrifuge PK 110 centrifuge (Thermo Electron Corporation).

A microwave system (Ethos Easy, Milestone) was used for the digestion of the residues of the extraction. All measurements of trace element concentrations were carried out using a 7800 ICP-MS Agilent in He mode.

Measurements

 $10 \ \mu$ g/mL internal standard solution of Bi, Ge, In, Li, Sc, Tb, Y (Agilent Technologies) and $1000 \ \mu$ g/mL multi-elements standard solution of Ca, Fe, K, Mg, Na, e $10 \ \mu$ g/mL di Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V, Zn (Agilent Technologies), were used for the analytical measurements, performed by 7800 Agilent ICP-MS.

Standard solutions for daily calibrations were prepared in the corresponding extracting solution and in the same dilution ratio used for the analysis of the extracted samples to ensure matrix matching.

Sequential extraction quality control procedure on CRM BCR 701

The results of the quality control analysis on the extraction procedure for the Certified Reference Material (CRM) BCR 701 according to the BCR sequential extraction procedure are shown in Table 4.11. The concentration values for each element (Cd, Cr, Cu, Ni, Pb and Zn) in each step of the sequential extraction are compared with the corresponding certified concentration values in each extraction step. In Table4.12 are shown: the element concentrations determined in the residue of the sequential extraction performed on CRM BCR 701, the sum of the concentrations of the extracted elements in each step of the procedure and in the residue, the total concentrations of each element measured in CRM BCR 701 and the recovery values (expressed as percentages) calculated for each element.

Step I	Cd	Cr	Cu	Ni	Pb	Zn			
		mg/kg							
CRM BCR 701 Values in this study	7.9±0.6	2.72±0.36	50.8±1.0	15.4±1.8	2.86±0.18	204±6			
Certified Values	7.3±0.4	2.26±0.16	49.3±1.7	15.4±0.9	3.18±0.21	205±6			
Step II	Cd	Cr	Cu	Ni	Pb	Zn			
CRM BCR 701 Values in this study	4.08±0.07	46.9±1.7	129±3	27.3±0.5	127±2	118±4			
Certified Values	3.77±0.28	45.7±2.0	124±3	26.6±1.3	126±3	114±5			
Step III	Cd	Cr	Cu	Ni	Pb	Zn			
CRM BCR 701 Values in this study	0.29±0.02	149±7	52±3	14.6±1.1	8.0±0.6	50±5			
Certified Values	0.27±0.06	143±7	55±4	15.3±0.9	9.3±2.0	46±4			

Table 4.11: Quality control analysis for each step of the SEP on CRM BCR 701 (Certified Reference Material). Comparison between the concentration values (mg/kg) of the elements extracted and measured in each step of the BCR sequential extraction procedure performed on CRM BCR 701 and the corresponding certified concentration values of each element in the related extraction step.

	Cd	Cr	Cu	Ni	Pb	Zn		
		mg/kg						
BCR 701 Residue	0.174±.01	118±1	45.1±6.8	49.5±6.5	24.4±.3	117 ± 12		
Σ (Step1+Step2+Step3+Res)	12.5	317	277	107	162	490		
CRM BCR 701	12.5±0.6	340±3	301±10	111±8	163 ± 2	493±20		
Recovery (%)	100	93	92	96	100	99		

 Table 4.12: Element concentrations (mg/kg) in the residue obtained at the end of the sequential extraction of CRM

 BCR 701. Sum (mg/kg) of the extracted elements in each step of the procedure and in the residue. Total

 concentrations (mg/kg) of the elements in CRM BCR 701 and recovery values (%) calculated for each element.

4.4 S.E.P. applied to Los Humeros and Phlegraean Fields geothermal soils

4.4.1 Introduction

As already stated, we decided to investigate soils collected in two different geothermic locations; therefore, soils were sampled in the geothermal area of Los Humeros in Mexico and in the Phlegraean Field geothermal area, in Italy. These two geographically far and different places were specifically selected in order to compare the results of a geochemical approach capable of taking into account the study of the trace elements mobility in geothermal soils. Moreover, the goal was to test and, then, suggest an effective and easy methodology that can be used worldwide in similar geological settings, as well as supporting decision makers in order to manage the environmental complexity of geothermal areas before and during the geothermal resource exploitation.

To date, there are scarce information on trace elements mobility and, in particular, of metal mobility in geothermal environments. With this research activity, as part of the GEMex project, we tried to fill the gap. In addition, we intended to increase the knowledge about the mobility in soils of some elements considered as potentially dangerous for the environment and for human health.

For the purposes of this study it was also necessary to find, for each sampling area in Mexico and Italy, two sites, placed at short distance from each other but showing two different situations: the first, characterized by the presence of current geothermal activity (as an example, existence of emissions, etc.). The second situation considers a soil in an area without any geothermal activity. The aim was to verify the possible influence of the presence of hydrothermal fluids, high temperatures, pHs extreme etc., on trace elements mobility in geothermal soils subjected to different conditions.

4.4.2 Los Humeros Geothermal soils geochemical properties

The Mexico geothermal soils were sampled by GEMex colleagues, who contributed to the WP4 regarding the activities of sampling campaigns in the field area of Los Humeros (Figure 4.3). For this partnership, special thanks go to the colleagues Matteo Lelli (IGC Pisa, Italy) and Ruth Alfaro Cuevas Villanueva (UMSNH, Mexico) who directly dealt with the selection of the sampling points, the sample collection and shipping to the ENEA's laboratories in Rome.

Soils were collected in two areas located at short distance away (about Km 2): Loma Blanca (soils LB1 3 LB2) and Xalapazco (soils XA1 and XA2). The Xalapazco area is characterized by the presence of a volcanic crater that is no longer active. Samples location is reported in Table 4.4.

For an exhaustive area description and for geological, geochemical and volcanological information please, refer to the Deliverables produced for the Gemex Project and, in particular, of GEMex Project, Task 4.3, Deliverable D4.3.

Unfortunately, the available data do not allow us to acquire an exhaustive geo-chemical characterization of these soils. Laboratory analysis however, gives evidence of the high acidity for all the considered soils because the highest pH value is close to 3.7. The lowest pH values correspond with the highest soil temperatures, highlighting the effect of the acidification produced by sulphur-rich geothermal fluids.

As for trace elements, there are distinctions, sometimes remarkable, in the concentration of the elements even within the same series of samples rather than between the LB and XA series (Table 4.4).

Among the elements that are mostly related to geothermal activity, we can underline arsenic, which is present with very low concentration, while a wide concentration range results for mercury. For this element, the maximum range is very high also considering the typical levels reported in literature in similar environments. (Tables 4.5; 4.6 and 4.7). As regards the relationship with the soil temperature, colder soils mark out for As enrichment, while Hg prevails in warmer condition.

As regards for the other elements analysed, data show very high Cr levels, especially in the XA soil. As for the other heavy metals, Ni, which is considered geochemically similar to Cr, displays extremely low concentrations and, in sample LB1, is below the detection limit for the procedure used. However, outliers are found in XA2 soil where Ni exhibits a concentration of 63.1 mg/kg and Cr of 120 mg/kg.

Los Humeros soils are characterized by extremely low levels of Fe and Mn, also compared to the typical concentrations for these elements in the world soils. Furthermore, Fe is mostly enriched in cold soils. This evidence is probably due to the prevalence of oxidation processes enhanced by the low soil temperature.

The main geochemical information available for these soils are summarized in Tables 4.3 and 4.4.

4.4.3 Phlegraean Fields Geothermal soils geochemical properties

The sequential extraction methodology was applied to four top soils, representative of the Phlegraean Fields geothermal area. In order to be representative, we considered several discriminating factors, such as top soil temperature, pH, location and soil usage. Some general information and geochemical analyses have been reported in Tables 4.4 and 4.5.

In the Phlegraean Fields the "hot" soils (Figure 4-6, Table 4.4) show a rather wide temperature range, between 75.5 and 113.6 °C, while for the "cold" soils (namely samples CFP5 and CFP7), the temperatures are quite similar, ranging from 9.4 to 9.7 °C, respectively.

Sampling was carried out at the end of the fall season, usually rich in rainfall while, in summer, at daytime, for the action of solar radiation, the soil temperature, even if not directly exposed to the action of geothermal fluids, can easily reach temperatures of 50-60 °C. It is evident that, during the year, the temperature, in this particular environment, is subject to a wide spatial and temporal variability as reported from monitoring stations data records (Figure 4-6).

Another important parameter that should be considered is the soil pH, which is always acid in "hot soils" (pH range 1.51 - 4.10) or weakly acid or close to neutrality, in "cold soils": samples CFP5 and CFP7 (pH= 6.08 and 7.10 respectively).

As regards trace elements, mercury shows rather high concentration levels, especially when compared with the typical values of the world's soils (Tables 4.6, 4.7, and 4.8). This anomaly also characterizes the geothermal soils of Tuscany, in particular in Mount Amiata geothermal area, one of the main and well-known world's geothermal sites, where the soils Hg levels are of the same order of magnitude of those considered in this work. (Baldi et al., 1988; Bargagli and Barghigiani, 1991; Bargagli et al., 1997).

The available data, although their wide variability, indicate that the Hg highest concentration levels account for soils with the highest temperatures. However, we point out the unexpected exception, such as that showed by the CFP3 sample, the "hottest" soil among those selected (113.6 $^{\circ}$ C), which has the lowest Hg level (0.87 mg/kg). This evidence could be justified by the uniqueness of this environment, characterized by extreme geochemical conditions. Here different chemical-physical processes coexist

and interchanges of chemical condition may occur: changes in pH, changes in redox conditions and Eh. Besides, these processes can also induce the removal or precipitation of mercury. This element, is released in different chemical forms, such as Hg (II), Hg (I) and Hg (0), that may origin during weathering in relation to pH/Eh conditions and/or to the presence of reducing species such as fulvic acids. The strong retention of Hg in soil is another factor that control its mobility. Furthermore, the effect produced by small-scale structural and morphological limitations (faults, diffuse fracturing, etc.) linked to local tectonics, should not be overlooked. In addition, it has been also observed that, in soils associated to active faults zones, Hg is about four times higher than that found in soils from non-active fault areas.

Arsenic does not show an unambiguous relationship with temperature. In fact, the lowest concentration value (2.07 mg/kg) corresponds to CFP4 soil (101° C) while both soils, classified as 'cold', display different arsenic levels that are similar to that of the hot soils. In this environmental setting, As mobility is probably strongly dependent on the changes in the redox conditions, while a lower effect is that related to pH (low) and temperature.

As regards the other considered elements (Cd, Cr, Cu, Ni, V, and Zn), if we take into account the geological reference framework, the concentration levels, including also the maximum values, are always below the limits considered excessive for soils (Table 4.6). Furthermore, as a rough approximation, it does not seem to be any relationship between the temperature and pH with the concentration of the elements in soil. Unfortunately, the limited number of samples did not allow us to achieve conclusions supported by a statistical significance. In the future, we will certainly try to fill this gap by resuming and extending sampling to other areas.

Arsenic does not show an unambiguous relationship with temperature. In fact, the lowest concentration value (2.07 mg/kg) was found in CFP4 soil, whose measured temperature was of 101°C, while for the soils, classified as 'cold', were measured different arsenic levels that are similar to those determined for the hot soils. In this environmental setting, As mobility is probably strongly dependent from the changes in the redox conditions, while a lower effect can be related to both pH (low) and temperature.

The CFP4 soil, placed inside a fumarolic area, stands out as "hot" soil, having a temperature of 101 °C and a pH of 1.51. The total concentrations of As Co, Cu, Fe, Mn, V, and Zn determined for CFP4 soil were lower than those found for the same elements in the CFP7 sample, a "cold" soil utilized for agriculture and characterized by a temperature of nearly 10°C and a pH of 7.10. CFP4 sample soil is also characterized by a very high concentration of Hg (89 mg/kg) especially if compared to the levels measured in the other soils.

On the other hand, CFP1 and CFP6 samples were collected in an area with strong gas emissions and for this reason, they are extremely hot, being their temperatures of 70.2 and 94.7° C, respectively. Finally, these soils are also both very acid with a pH of 3.2 and 4.1, respectively.

4.5 SEP (Sequential Extraction Procedure) discussion

In order to provide a more detailed discussion of the results obtained with the extraction of the soil samples with the BCR sequential extraction procedure and, at the same time, to make easier its reading, we decided to describe the mobility of the elements for each single sample and separately, for Mexico and for the Phlegraean Fields geothermal soils.

4.5.1 Los Humeros geothermal soils

XA1 Soil

In this soil sample, the complete Zn extraction (Figure 4-8), is obtained already in the first step of the BCR procedure. However, it should be highlighted, that the total content of Zn, measured in this sample, is extremely low (1.21 mg/kg), therefore, the high mobility of this element does not represent a risk for the environment.

In the first step, corresponding to the exchangeable and weakly adsorbed fraction, the extraction of about 60% of the Co and 28% of the Cu is also achieved (Figures 4.9 and 4.10). Furthermore, in the same step, a relatively high Fe and Mn mobility can be observed. Both elements are extracted for about 40% of their total content. In sample XA1, the total concentrations of Fe and Mn are quite low (Figures 4.11 and 4.12), especially if we consider the levels estimated typical for these elements in soils of volcanic origin. Therefore, this highlighted mobility allows us to hypothesize that Fe and Mn are present in this soil as amorphous compounds, such as salts or carbonates, characterized by weak and easily dissociable chemical bonds.

In the same sample, the results obtained from the extraction of Cr, Pb, and V point out a very low mobility for these elements, which are found enriched mainly in the residue that is obtained at the end of the sequential procedure (Figures 4.13; 4.14 and 4.15).

Cadmium (Figure 4.16) is preferentially enriched in the residue and shows a modest mobility. In fact, about 10% of the total content is extracted in each of the three steps of the extraction procedure.

A total concentration of 0.327 mg/kg was measured for As in sample XA1 (Figure 4.17). This value, as a first approximation, is particularly low if we consider the volcanic origin for the parent material of this soil. The low As concentration can be also associated to several factors such as: a possible removal from the soil triggered by the action of gaseous emissions; the high soil temperature and the presence of circulating acid solutions, as evidenced by the low pH values. Furthermore, although is well known the remarkable geochemical affinity between arsenic and iron, since iron (as Fe-oxy-hydroxides) are the main sequestration agents (Bundschuh and Maity, 2015), the low Fe concentrations in this sample, probably, does not foster this geochemical process. In addition, arsenic shows poor mobility since it is extracted for about 15 and 5% of the total content, respectively, in steps 1 and 3 of the sequential extraction procedure.

XA2 Soil

The sample XA2 differs from XA1 for the lower soil temperature (12.5 °C and 64.5, respectively) and for a relatively higher pH value (3.69 and 1.18, respectively, Table 4.3) Also for this sample, trace elements are preferentially enriched in the residual phase of the sequential extraction procedure.

The elements that show a relative higher mobility are As, Cd, Mn and U (Figures 4.17; 4.16; 4.12; 4.18). In particular, Cd and U (Figures 4.16 and 4.18) evidence a mobility of about 25 and 40% respectively, of their total content, distributed in all three steps of the procedure. For Mn and As, the availability was about 30%, of their total content, and almost exclusively attributable to steps 2 and 3 of the sequential extraction procedure. With lower percentages, Cu, Cr, Pb and Zn (Figures 4.10, 4.13, 4.14 and 4.8) were extracted mainly in the second and third steps. In this sample no one element, with the exception of the Cd, extracted for about 8%, was removed in the first step of the procedure to a significant amount. This evidence suggest that these elements are mainly associated with iron and manganese oxides and/or hydroxides and, to a lesser extent, also to the organic fraction.

LB1 Soil

As regards the Loma Blanca soils (LB1 and LB2), they show significant differences for the soil temperature (92.6 and 11.3 °C, respectively) and for the pH values (1.52 and 3.71, respectively). In general, data show that in LB1, the total concentration levels of some elements (such as As, Co, Cr, Cu, Fe, Ni, Pb and V) are lower than those measured in soil LB2 (Table 4.4).

In LB1, the metal availability is very low. In fact, As, Cd, Cr, Mn, U, and V are present almost exclusively in the residual phase obtained at the end of the three steps of the sequential extraction. (Figures 4-17, 4-16, 4-13, 4-12, 4-18 and 4-15).

Pb is extracted for about 60% of its total content almost exclusively in the second step, highlighting the prevailing association with the reducible fraction (Figure 4.14). However, this relatively high mobility does not represent an environmental risk, since the total Pb concentration determined in this sample is equal to 10.8 mg/kg, a value that falls within the typical concentration range for soils of volcanic origin (Table 4.6).

Concerning Zn, the extractable fraction is obtained essentially in the third step and corresponds to about 35% of the total content of zinc in this soil. This allows us to hypothesize that zinc is mainly associated with the organic fraction (figure 4.8).

For Co, we can suggest that it is mainly associated to the organic phase of the sample soil as it is extracted for about 20% of its total content, in the third step of the BCR sequential extraction (Figure 4.9).

Arsenic and V are found almost totally in the residue, thus exhibiting a low environmental mobility. In fact, only a negligible fraction of their total content was extracted in the third step of the BCR (Figure 4.17 and 4.15).

In the LB1 sample, the percentages extracted for Fe and Cu, in the first step of the BCR represent, respectively, about 10 and 20% of their total content (Figures 4.11 and 4.10).

In summary, in the LB1 sample the elements that show lower mobility are: As, Cd, Cr, Mn, U, and V. However, a negligible percentage of extraction is observed, always less than 10%, also for As, Cr and V, which are extracted in the third step of the BCR and for Mn, extracted in the first step.

Moreover, in this sample, also the uranium availability is negligible (Figure 4.18). In fact, for this element it is not observed any extraction in the steps of the sequential extraction procedure. This experimental evidence is, however, very important because for Uranium, there are few studies about its environmental availability and rare evidences exist about its behaviour in geothermal soils. Therefore, these data, discussed on behalf of the Gemex project, could represent a reference point for future studies.

LB2 Soil

LB2 sample is an acid soil (pH 3.7), has a low temperature $(11.3 \circ C)$ and stands out by a general poor mobility for all the studied elements, except for Co and U. In fact, they are extracted with percentages of about 20% of the respective total content, mainly in step 3, in the case of Co, and in steps 2 and 3 for Uranium. In addition, since the total Co and U concentration levels are rather low, the mobility exhibited by these two elements does not represent any possible hazard for the environment (Figures 4.9 and 4.18).
As regards the other considered elements, a mobility of about 10% of their respective total content, was determined for Cu and Mn (Figures 4.10 and 4.12), while for As, Fe, Pb, and Zn mobility results negligible, being less than 5%. (Figures 4.17; 4.11; 4.14, and 4.8).

The outcome concerning Cr and V mobility (Figures 4.13 and 4.15) are comparable to that founded for the LB1 sample. These elements, due to their chemical-physical characteristics and for the complexing e/o redox properties of the reagents used in each steps of the BCR, are not easily extracted from these soils except for very low percentages and, in any case, less than 5%, of their respective total content, in the third step.

Likewise, as in LB1 sample, Cd, whose total content in this soil is quite low (0.180 mg/kg), does not display any environmental concern since it was not extracted in any of the steps of the extraction procedure and it is found completely in the residue of the whole extraction procedure (Figure 4.16).

4.5.2 Conclusion: Los Humeros geothermal soils

The application of the BCR sequential extraction procedure on soil samples in the geothermal area of Los Humeros allows us to achieve the following conclusions:

1. The mobility study carried out on the trace elements of environmental importance evidences a general low availability of these metal elements in the occurring chemical-physical conditions. In fact, usually, the main percentage of the metals is found in the residue, that is the fraction obtained at the end of the SEP (Sequential Extraction Procedure).

2. As regards elements such as Cd, Cr, and V, the observed mobility is completely negligible in all the investigated soil samples.

3. Pb is characterized by a low availability and only in LB1 sample was significantly extracted in the second step of the SEP. This is in accordance with the usual geochemical behaviour that entails Pb to be associated with oxi-hydroxides of Fe and Mn.

4. Ni total concentration in samples XA1, LB1 and LB2 is extremely modest and close to quantification limit (LOQ = 0.1 mg/kg). As a consequence, it was not possible to estimate Ni distribution between the different fractions obtained with the three steps of the BCR.

5. In sample XA1 the total concentration levels of Fe, Mn and Zn are particularly low compared to the concentrations considered typical for these elements in volcanic soils. However, they are all extracted in high percentage, already in the first step of the SEP in which is used acetic acid 0.11M. Some soil parameters as temperature and pH, together to the action of the hydrothermal fluids, might enhance the formation of amorphous minerals where Fe, Mn and Zn are weakly bounded and, then, easily mobilized. This could also explain the low total content found for these elements in XA1 soil.





Figure 4-8: Extractable Zn after the application of SEP to Los Humeros geothermal soils

Figure 4-9: Extractable Co after the application of SEP to Los Humeros geothermal soils



Figure 4-10: Extractable Cu after the application of SEP to Los Humeros geothermal soils



Figure 4-11: Extractable Fe after the application of SEP to Los Humeros geothermal soils



Figure 4-12: Extractable Mn after the application of SEP to Los Humeros geothermal soils



Figure 4-13: Extractable Cr after the application of SEP to Los Humeros geothermal soils







Figure 4-15: Extractable V after the application of SEP to Los Humeros geothermal soils





Figure 4-16: Extractable Cd after the application of SEP to Los Humeros geothermal soils

Figure 4-17: Extractable As after the application of SEP to Los Humeros geothermal soils



Figure 4-18: Extractable U after the application of SEP to Los Humeros geothermal soils

4.5.3 Phlegraean Fields geothermal soils

The Flegrean Fields is one of the most famous world's volcanic area and has a long history being inhabited since ancient times. For this reason, human intervention has heavily influenced the evolution and the landscape morphology. The high fertility of the volcanic soils was well known by Romans and, before, by Greeks. All this has always represented a richness for the territory but, at the same time, the strong and long-lasting anthropic pressure has reduced the possibility to find real "natural" areas and soils for our purposes. In addition, this land is one of the most intensely populated among the Italian territories and with respect the world, because the population density ranges from 2500 to 8000 inhabitants per km².

The location map of the samples is shown in Figure 4-4, while the surface temperature values are shown in Figure 4-6.

The total concentration levels of some elements measured in the geothermal soils collected from the Flegrean Field are reported in Table 4.4.

The soil samples from the Flegrean Fields, chosen to be studied by the BCR extraction procedure, were selected always with the purpose of representing some typical situations related to the geothermal environment. The aim was also to compare the results of the BCR extraction procedure obtained for these geothermic soils with soils collected in other geothermal world areas, and in particular with the Los Humeros geothermal soils.

The CFP4 sample was collected inside an active fumarolic area characterized by high average temperatures (101° C and very acid pH value, 1.51).

Sample CFP6 was collected in an extremely hot area where, at the time of sampling, the temperature was 94.7 °C, the soil pH was 4.10 and there was also moderate fumarolic activity. Due to its location, this sample can be considered as intermediate between CFP4 and CFP1 soils. This latter was collected from a contiguous area with evident fumarolic activity and can be considered representative of a transition zone between sites characterized by extreme soil temperature values.

Finally, the CFP7 soil does not have thermal anomalies as it was sampled in an area without any fumarolic activity. In fact, it has been used for agricultural activities for a long time.

Table 4.4 shows the total concentration levels of the elements determined in the four soils selected to be extracted by the BCR sequential extraction procedure.

From these data, it is evident that the total concentrations for most of the elements in CFP4 sample, a soil developed in an area with intense geothermal activity, are very low. In particular, very low total concentration levels were found for As, Cu, Fe, Mn, Pb and Zn, especially if compared with the levels found in other soils from the same area.

Total Hg concentration in Soil CFP4, 89.0 mg/kg, is a very high content, probably due to hydrothermal fluids contribute.

Compared to CFP4 soil sample, the total Hg concentrations measured in the other samples are significantly lower, probably because of the removal of this element caused by the action both of hydrothermal fluids and rainfalls. Furthermore, the Hg removal is also fostered by the low pH soil.

Even the modest concentration levels found for elements such as Fe and Mn, that are usually present in soils with high concentration values, that are commonly expressed as percentages, can be explained by presuming their removal from the "system" owing to the combined action of acidity and hydrothermal fluids.

In this regard, the temperatures measured in CFP6 and CFP1 soils (94.7 and 70.2 $^{\circ}$ C, respectively) may cause volatilization and consequent removal of elements particularly sensitive to temperature such as As and Hg. Both, in fact, exhibit relatively low total concentration levels, especially considering that they are soils developed in a volcanic environment.

CFP4 soil, sampled in an area with intense geothermal activity and extracted by the sequential extraction procedure, shows a low mobility for Cd, As, V and U (Figures 4.19; 4.20 4.21; and 4.22). In fact, these elements are found only in the residual phase obtained at the end of the sequential extraction procedure. The low mobility of these elements is probably related to two different factors. The first is represented by the tendency for these elements to be preferentially retained within the crystal lattices of primary minerals. The second, is related to the very low concentration values measured for these elements in this soil sample. The extremely low contents of these elements reduce the possibility that the percentage in excess might be mobilized and, then, becoming potentially available.

Among the elements that exhibit greater mobility and, that are extracted in the first step of the BCR procedure, can be considered Cu, that is extracted for about 15% of its total content (Figure 4.23), while Fe, Mn and Cr are extracted for a negligible fraction whose value does not exceed 5% of their respective total content in the soil sample (Figures 4.24; 4.25 and 4.28).

In CFP4 soil, Pb displays a high mobility (Figure 4.26). In fact, it is extracted for about 25% mainly in the second step and, then, in the third step, for about 10%, of the sample total content. It is likely that this element is mostly associated with the iron and manganese oxides that represent the reducible fraction extracted in the second step of the BCR procedure.

Zinc, Cr and, for about 5% of the total content, Co, all are extracted with the third step of the sequential extraction procedure, evidencing that they are preferably associated with the soil organic fraction (Figures 4.27, 4.28 and 4.29).

The CFP6 sample, characterized by a surface temperature, at the time of sampling, of 94.7 °C and a pH value of 4.1, represents a soil which, compared to the other Flegrean Fields samples exhibits the greatest mobility for all the considered elements. In fact, Cd, Mn, Zn and, to a lesser extent, As, Co and Cu, are extracted in all the steps of the BCR procedure (Figures 4.19; 4.25; 4.27; 4.20; 4.29 and 4.23). In particular, Mn and Cd were extracted with similar percentages (about 30-35% of their total concentration in the sample) in step 2, in which the reducible fraction is preferentially extracted. In the same sample, the percentage of Cd extracted in the third step is about twofold (5%) compared to that extracted for Mn. Uranium and copper (Figure 4.22 and 4.23), are extracted at higher percentage only starting from the third step of the procedure, probably because they are associated with the soil organic fraction. From these data arise that uranium, in the chemical-physical conditions that characterize this sample soil, results as one of the most available elements in contrast to the general behaviour observed for the other soil samples, in which uranium is characterized by a scarce mobility. In fact, it is observed that U is preferentially enriched in the residual phase of the sequential extraction procedure.

Concerning Pb and Cr (Figures 4.26 and 4.28), they are extracted for about 15 and 20%, respectively, of their total content. In detail, Cr is extracted in the third step of the BCR, while Pb in the second step. These results indicate that, in these conditions, Cr is mainly associated with the organic soil fraction, while Pb with the easily reducible fraction.

In the Flegrean Fields area, V and Fe show low concentration values and a wide variability (Figures 4.21 and 4.24). These elements are extracted in the second and third steps of the SEP with overall percentages of 20 and 10% of their total content in soil sample, respectively. Besides, they also show a low mobility, as testified by their preferential occurrence in the residual phase of the SEP.

The sample CFP1 is representative of an area considered as transitional between with hot and cold soils. Extraction data evidence negligible mobility for all the elements with the exception of As, Cu and Pb (Figures 4.20 4.23 and 4.26). Arsenic and lead have been extracted for about 20% of their total content in this sample, mainly in the second and third steps of the procedure, while Cu is extracted for 20% of the total content in the third step of the BCR. In this sample As and Pb are mainly associated with iron and manganese oxides, while Cu with the soil organic fraction. Furthermore, Arsenic is removed with percentages that are comparable to those calculated for the CFP6 sample, thus showing identical environmental mobility and highlighting, in both samples, the tendency to be associated with iron and manganese oxides.

Even the agricultural soil sample CFP7 does not show a significant mobility of the studied elements. In fact, most of them are present for about 80%, of their total content measured in the sample, in the residue.

Among the relatively more mobile elements, we point out Mn, Zn and Cd. The first two have been extracted across all the three steps of the sequential extraction, while Cd is extracted only in the first and second step. In this soil, Pb is extracted mainly in the second step of the BCR (about 20% of its total

content in the sample), while its extractability in the third step is negligible. In all Flegrean soils, Pb evidences a similar availability degree after the application of the BCR extraction procedure, notwithstanding the differences in pH and soil temperature.

Finally, Cr reveals the known low environmental mobility, being extracted for about 10%, of its total content, in the third step of the BCR extraction evidencing a behaviour similar to that of the other soils investigated (Figure 4.28).

4.5.4 Conclusion: Phlegraean Fields geothermal soils

Results obtained by the extraction of the Flegrean Fields geothermal soil samples with the BCR sequential extraction procedure highlight the following considerations:

1. A low mobility of all elements: this is evidenced by the high percentage determined in the residual phase of the sequential extraction for each considered element.

2. Pb is extracted in a quite modest percentage mainly in the second step and, to an even lesser extent, in the third step of the sequential extraction. Therefore, it can be assumed that this element is preferentially associated with iron and manganese oxides and hydroxides and, in some cases, with the organic fraction.

3. Arsenic shows a very scarce availability, especially when its total concentration levels determined in the soil samples are very low. In fact, it is extracted in the second and, to a lesser extent, in the third step of the sequential extraction.

4. Vanadium shows a geochemical behaviour similar to that shown by arsenic. In fact, its mobility is very low, being extracted in the second and, to a lesser extent, in the third step of the BCR procedure. For this element, we can suggest a possible interaction with oxides and organic fraction.

5. Copper is mainly extracted in the third step of the sequential extraction, highlighting that this element is mostly associated with the soil organic fraction.

6. Chromium is characterized by a low mobility and, when results to be extracted, is present especially in the third step of the extraction procedure.

7. Zinc, although shows a low mobility, when extracted, is associated with the organic fraction (third step of the BCR). However, in some conditions, where is weakly associated to the soil components, a partial extraction is observed in the first step, where a weak acid solution is utilized as extractant.

8. Cd shows a poor availability. However, in those situations where displays a greater mobility, it is extracted in all the three steps of the BCR. Usually, the concentration levels of Cd in soils are extremely low, less than 1 mg/kg. Therefore, the risk of environmental hazard, even in the case of slightly greater mobility, is negligible.

9. Both Fe and Mn evidence a low mobility. However, when they are present in soil as amorphous phases which can be easily mobilized, they are mainly extracted in the first and second step of the BCR.

10. The concentration levels of total uranium range between 5 and 9 mg/kg; these values are similar to the world soils typical concentration ranges, but they are lower than the typical levels for soils from geothermal environment. In CFP6 sample, uranium shows a relevant mobility, being extracted

preferentially in the third step for 50% of its total content in the sample. However, even in this case, the modest U total concentration ensures that, despite the not negligible availability, it does not constitute a potential environmental hazard.



Figure 4-19: Extractable Cd after the application of SEP to Phlegraean geothermal soils



Figure 4-20: Extractable As after the application of SEP to Phlegraean geothermal soils



Figure 4-21: Extractable V after the application of SEP to Phlegraean geothermal soils



Figure 4-22: Extractable U after the application of SEP to Phlegraean geothermal soils



Figure 4-23: Extractable Cu after the application of SEP to Phlegraean geothermal soils



Figure 4-24: Extractable Fe after the application of SEP to Phlegraean geothermal soils



Figure 4-25: Extractable Mn after the application of SEP to Phlegraean geothermal soils



Figure 4-26: Extractable Pb after the application of SEP to Phlegraean geothermal soils



Figure 4-27: Extractable Zn after the application of SEP to Phlegraean geothermal soils



Figure 4-28: Extractable Cr after the application of SEP to Phlegraean geothermal soils



Figure 4-29: Extractable Co after the application of SEP to Phlegraean geothermal soils

4.6 General conclusion

On the occasion of the GEMex project, the BCR sequential extraction procedure has been first applied to geothermal soils to highlight the availability of PHE (Potential Harmful Elements) in this particular environment.

Surface soil samples from two known geothermal areas were studied. The aim was to verify whether the proposed working method could provide a valid, reproducible and comparable methodology to be used in different geothermal contexts. Furthermore, it has been verified that the application of sequential extractions for the first time on geothermal soil samples represents a valid tool for rapid characterization and subsequent environmental management of those areas.

In fact, for all the elements, there is a relatively modest mobility despite the environmental conditions that characterize both sites: low pH values, high soil temperature and the presence of chemically aggressive fluids. The above mentioned conditions, indeed, usually favour the mobility of the elements and make them potentially more available in the environment.

The low mobility of most elements is also evidenced by the tendency to accumulate in the residue. This suggests that most of the total content for these PHE is strongly associated with the soil matrix and that the mobile fraction is generally low in the chemical-physical conditions of these soils.

Similarities in elements behaviour occur for both sites.

Pb shows low availability and results to be associated with iron and manganese oxides and hydroxides.

As, Cu, V and Cr are all hardly available and, sometimes, evidence some mobility only from the third step of the SEP.

Cd shows poor availability in both sites where it is present with very low concentrations. This greatly reduces its environmental hazard even if in case of changes in external conditions that could improve mobility.

Low mobility affects also Fe and Mn. One of the reasons is the relatively low concentration in these soils. However, increase in mobility can be induced by the action of hydrothermal fluid, changes in pH, Eh and temperature that could enhance the formation of amorphous mineral.

At the end of this study within the GEMex project, we can conclude that the application of a sequential extraction methodology on the soils from Los Humeros and the Phlegraean geothermal area, highlighted the effectiveness of the methodology adopted concerning the evaluation of the mobility of some potentially toxic elements in geothermal soils. In fact, despite the diversification that characterizes the two areas, the studied elements evidence a similar behaviour as soils are subjected to the same sequential extraction procedures. This shows that this procedure can also be applied in different conditions providing practical indications for understanding and managing some environmental problems related to the exploitation of geothermal energy also through EGS technology.

4.7 References

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5 Tracer tests for monitoring Superhot Hot Geothermal Systems

by Jiri Muller, IFE

5.1 Introduction

This report deals with tracer field tests using the new tracer developed under the GEMex project. It belongs to the Task 8.4 which is part of WP8. The development, testing and properties of the new tracer have been described in more details in the deliverable belonging to the Task 4.3.

The goal of this report is to provide guidelines on how to perform field tests with the new tracer. The actual performance of the field tests lies outside the scope of GEMex project. However, we have been in contact with several operators world-wide who have been interested in testing the new GEMex tracer in collaboration with IFE. In particular operators on Iceland and New Zealand have shown interests and they are preparing their own field studies with the GEMex tracer in their high temperature fields. However, the results of these tests will be known after the end of the GEMex project. At the beginning of the GEMex project there was also an interest from the Mexican partners to perform field tests in their high T fields, but this operation has been postponed. However, we are continuously in touch with our Mexican colleagues and we are prepared to collaborate with them on the field tests also after the official closure of the GEMex project.

5.2 Background

In Task 4.3 of the GEMex project seven different tracer candidates were tested for thermal stability and flooding properties. The tests showed that the inorganic anion perrhenate (ReO_4^{-}) was stable above 250°C and had suitable flooding properties. Other inorganic anions like MoO_4^{2-} and WO_4^{2-} , that were also tested, were not stable at this temperature when Basalt rock was present in the test vials. Organic tracers like naphthalene and pyrene sulfonates have been applied as water tracers in geothermal reservoirs, but these compounds may not be sufficiently stable above 250°C. Water soluble Re in vials containing Basalt rock was stable at the maximum test temperature of 350°C. In flooding experiments with the same rock material at 375°C, which was the highest test temperature applied, there was no sign of reduction of the Re recovered in the eluted fractions, and the Re was eluted in about the same volume as the ideal water tracer tritiated water. The response curves from the experiment are shown in Figure 5-1.



Figure 5-1: Response Curves, 42 cm x 8 mm Column filled with Basalt rock, 240 bar, 375 °C

By analysing solutions of perthenate that had been exposed to the sulphur containing Basalt rock particles at temperatures above 250°C, it was found that the ReO_4^- ions had partly been transferred to ReOS_3^- . The two anions could be analysed using liquid chromatography (HPLC) in combination with ICP-MS. A chromatogram from the analysis is shown in Figure 5-2.



Figure 5-2: HPLC-ICP-MS Analysis of Re species in Test Solution with ReO4- Exposed to 250 °C with Basalt Rock

The presence of the ReO_3S^- ion was confirmed by liquid chromatography mass spectrometry analysis (LC-MS). H₂S released from the Basalt rock particles can react with perrhenate as shown in Figure 5-3.



Figure 5-3: H₂S reaction with perrhenate

The ReO_3S^- is also soluble in water and the flooding experiments showed that the sulphur containing anion had similar flooding properties as the perrhenate. When H₂S is present and the temperature is above 250°C, the above reaction may occur and even go further so that more of the oxygen atoms are replaced by sulphur. The concentration of Re in the solution will however not be changed and the flooding properties will remain the same.

Rhenium is a precious metal and perrhenate salts are therefore rather expensive compared to organic tracers like the naphthalene sulfonates. The natural concentration of Re in produced geothermal water will normally be extremely low. Analysis of formation water from some petroleum fields on the Norwegian continental shelf showed that the Re-concentration was less than $50\mu g/m^3$ (ppt). Metal elements like Re can be analysed using inductively coupled plasma mass spectroscopy (ICP-MS) The detection limit that can be achieved using this technique for water solutions of Re is extremely low. With the newest generation of ICP-MS instruments a detection limit below 10 ppt should be achievable. Such low detection limits are however not possible in brine solutions since the high concentration Na will interfere with the signal from the Re and high salt contents may also plug the sample inlet system. IFE has therefore developed a method for removing NaCl and other salts from such samples. The low detection limits that can be achieved for perrhenate in water solutions using ICP-MS cannot be achieved for the organic tracers like the naphthalene sulfonates even when using the presently most advanced techniques available such as liquid chromatography mass spectrometry (LC-MS) or gas chromatography mass spectrometry (GC-MS). The detection limit that can be achieved for the organic tracers will normally be about 10 times higher. In terms of tracer cost the perrhenate salts can therefore compete with the less expensive organic tracers since a smaller amount will be required for injection in the field.

5.3 Preparation of tracer solution for field injection

Ammonium perrhenate (NH₄ReO₄) is the Re-salt which has the lowest price on the market. The solubility in water is about 60g/l at 20°C (6kg/100 litre). The amount of tracer required to be injected for the field test will depend on the water production rate and the distance between injection well and sampling well. Based upon tracer field tests in Dixie Valley (Ref. 1 and 2), the necessary tracer amount of NH₄ReO₄ for a similar field should be in the order of 5-10kg. The amount of the aminonaphthalene sulfonate applied in the Dixie Valley filed tests was 100kg and the detection limit was reported to be 500 ppt. Since perrhenate can be detected at a level more than 10 times lower, an injection of 5-10kg should be sufficient for such an application. If a tracer amount of 5-10 kg is to be applied, the salt can

easily be dissolved in 250-500 litres of water. The solution in the container must be thoroughly stirred until all salt particles are dissolved. A higher amount of tracer will require an equivalent larger volume of water for dissolution. The whole volume of tracer solution should be injected in the well, and the pump should be flushed with water which should also be injected after injecting the tracer solution.

5.4 Calculation of tracer amount for injection

As mentioned above the amount of tracer required for injection will depend upon the water production rate, the total dilution volume, the flow pattern (inhomogeneous or directional flow) and the detection limit. Assuming a water production rate of ~1000m³/24hrs and a detection limit of 20ppt of the metal element ($20\mu g/m^3$), 20mg tracer dissolved in that volume should be detectable. Since the elution of the tracer is expected to be dispersed over perhaps more than one year period (500days), and it is preferable for the precision of the analysis that samples have a higher concentration than the detection limit level, a factor of 500x10 is recommended, giving an amount of 100g of the tracer element. Since far from all the injected water is back produced, another factor of 10 is recommended, giving a tracer amount of 1000g of the element, which corresponds approximately to 2kg of the tracer salt required for each field injection. Higher water production rates than $1000m^3/24hrs$ will require higher tracer amounts injected.

5.5 Tracer cost

The price of the ammonium salt of the tracer can vary a lot depending on quantity ordered and the purity of the chemical. A high purity chemical is not required for such field applications and the tracer should normally be available at a price of less than 2000 US\$ per kg. If the perrhenate salt can be bought for USD 1000 per kg, the tracer costs will not be very much higher than what would have been required if a naphthalene sulfonic acid salt was applied since the price for such chemicals will usually be in the order of USD 100/kg and 1/10 of the amount of the perrhenate salt is required.

5.6 Safety considerations

 NH_4ReO_4 is not regarded as hazardous but precautions using gloves and eye protection as described in enclosed safety data sheet should be taken. A safety data sheet for NH_4ReO_4 is enclosed in the attachments.

5.7 Collection of water samples for analysis

The samples can be collected in clean glass or plastic bottles. 200 ml of water sample in each container is sufficient for analysis. No other chemicals should be added to the samples after collection. The samples can be stored at room temperature.

5.8 References

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6 Conclusion

In order to characterise and monitor the evolution of the physical and chemical properties of the deep superhot reservoir of the Los Humeros geothermal system the following methods are proposed to be applied before and during drilling the first deep well, as well as during future exploitation:

- Continuing state of the art geological, geophysical, geochemical, production monitoring and reservoir testing practices, that have been or are currently being applied in Los Humeros
- Introduce vertical seismic profiling (VSP), seismic while drilling (SWD) and optical fibre DAS seismic monitoring methods
- Carry out tracer tests using new high temperature resistant tracers
- Monitor the mobility of potential harmful elements (PHE) in the soil
- Test new innovative materials and steam scrubbing methods for corrosion and scaling inhibition and steam purification, during production of superhot geothermal fluids

7 Acknowledgements

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Additional information available on http://www.gemex-h2020.eu/index.php?lang=en.

8 Annex: Thermal loop at superhot systems

by Dimitrios Mendrinos and Constanttine Karytsas, CRES

The objective of this annex is to make recommendations for the surface thermal loop of a deeper exploratory well to be drilled in Los Humeros, which is expected to tap a supercritical geothermal reservoir of pressures and temperatures much higher than the ones recorded in existing wells.

8.1 Expected superhot well properties

In Los Humeros geothermal system, the average well produces two phase fluid of 2600 kJ/kg specific enthalpy at 20 bar wellhead pressure, delivering 8 kg/s of steam with 3.86% non-condensable gasses (3.26% CO2 and 0.37% H₂S) and steam condensate pH of 7.2.

The hottest well integrated in the power plant, delivers superheated steam of 283 °C temperature, 40 bar pressure and 2900 kJ/kg specific enthalpy. The steam condensate has a pH of 4.47, compared to 2.62 of IDDP-1.

A deep well, down to more than 5 km depth drilled at Los Humeros is expected to yield highly more corrosive and abrasive fluids than standard high enthalpy wells, due to entrained acid gases (HCl and HF) and silica. Non condensable gases (CO_2 and H_2S) should be in much less concentration. Very few such wells are available worldwide, the most important of which are IDDP-1 and IDDP-2.

The thermodynamic properties of superhot fluid produced by well IDDP-1 are presented in Figure 8-1 and in Table 8.1. The composition of its gas phase is shown in Table 8.2, while the most important dissolved species of its steam condensate are presented in Table 8.3. Tables 8.1, 8.2 and 8.3 also include the thermodynamics and steam composition of Los Humeros wells currently connected to the power plant and newly drilled dry steam wells in Los Humeros.

	Utilised wells in Los Humeros	New dry steam wells in Los Humeros	IDDP-1
Fluid type	88% steam 12% brine	superheated steam	superheated steam
Max pressure	68 bar	90 bar	150 bar
Max Temperature	340 ⁰C	308 ⁰C	450 °C
Steam flow rate	8 kg/s	10 kg/s	48 kg/s
Pressure	20 bar	40 bar	45 bar
Sp. Enthalpy	2600 kJ/kg	2900 kJ/kg	3100 kJ/kg

Table 8.1: Thermodynamic properties of fluid produced from existing Los Humeros wells compared to the ones of IDDP-1; a 5-7 km deep well drilled in Los Humeros is expected to yield superheated steam of higher temperature, pressure, mass flowrate and enthalpy.



Figure 8-1: Production characteristic curve of IDDP-1 well; a new 5-7 km deep well drilled in Los Humeros is expected to have similar production features with well IDDP-1 as a first approximation

	Utilised wells in Los Humeros	New dry steam wells in Los Humeros	IDDP-1
Total NCG	3,88%	3,86 %	0,1081 %
CO ₂	36150 ppm	32550 ppm	732 ppm
H_2S	1900 ppm	3700 ppm	339 ppm
N ₂	300 ppm	1900 ppm	16 ppm
H ₂	2 ppm	154 ppm	10 ppm

 Table 8.2: Composition of vapour phase produced from existing Los Humeros wells compared to the one of IDDP-1; a

 5-7 km deep well drilled in Los Humeros is expected to yield superheated steam with much less non-condensable gases.

	Utilised wells in Los Humeros	New dry steam wells in Los Humeros	IDDP-1
Condensate pH	7.2	4.47	2.62
HCl	-	n.a.	95.6 ppm
HF	-	-	7 ppm
NH ₃	150 ppm	41 ppm	0.14 ppm
FeCl ₂	-	19 ppm	19 ppm
В	130 ppm	958 ppm	1 ppm
SiO ₂ (silica)	87 ppm	22 ppm	100 ppm
S ₈ (sulfur)	-	-	72 ppm
remark	Moves to brine	Only steam phase	Only steam phase

Table 8.3: Main dissolved species in steam condensate produced from existing Los Humeros wells compared to the one of IDDP-1; a 5-7 km deep well drilled in Los Humeros is expected to deliver extremely corrosive fluid due to entrained acid gases of HCl and HF, with a strong scaling tendency of silica and elemental sulphur.

8.2 Experience with corrosion inhibition and steam purification

In Los Humeros geothermal plant, continuous Injection of K_2CO_3 with Amine based inhibitor at the two phase pipeline, upstream of a dry steam well line connection as shown in Figure 8-2, has been successfully practised, resulting in reliable operation with zero scaling and zero measured corrosion.



Figure 8-2: In Los Humeros, injection of inhibitors at the two phase line before the intersection of the H43 steam line, effectively mitigated corrosion allowing the integration of superheated steam wells into the power plant.

The following thermal loop configurations for the exploitation of ultra-hot geothermal wells are proposed in the literature, each one aiming in a different method for facing corrosion, scaling and steam purification issues:

- (i) central heat exchanger with binary plant as, the configuration of which is shown in Figure 8.3,
- (ii) steam purification by wet scrubbing and condensing power plant as shown in Figure 8.4, and
- (iii) steam purification by dry scrubbing and condensing power plant as of Figure 8.5.

Of these configurations, only the wet scrubbing one has been tested in superhot geothermal wells, namely in IDDP-1 well and for limited time only. The main conclusions drawn from the IDDP-1 wet scrubbing experience are:

- The acid gas in the steam could effectively be scrubbed away with either brine, or condensate or cold groundwater.
- The silica dust and the dissolved silica in the steam precipitated when the pressure was reduced and was effectively washed from the steam into the scrubbing water.
- The sulfur in gaseous form, in IDDP-1 steam however, could only be scrubbed from the steam with alkaline water.



Figure 8-3: Configuration of a binary plant with main heat exchanger and wet scrubbing with brine



Figure 8-4: Configuration of a flash steam plant with wet scrubbing with steam condensate



Figure 8-5: Configuration of a flash steam plant with dry scrubbing

8.3 Materials selection

At present, there is no metal or alloy that can guarantee corrosion free operation with the aggressive superhot geothermal fluids. An evaluation carried out by the authors based on available information in the literature is presented in Table 8.4. Aluminium is subject to intense pitting corrosion, copper and its alloys are attacked by H₂S, nickel is also attacked by H₂S and metal chlorides, while even the most exotic iron/steel stainless alloys are subject to corrosion above 150 °C. Titanium shows the highest resistance and corrosion free operation up to 300 °C.

Plastic lining materials commonly used for corrosion protection are not stable at such temperatures. Therefore, development and testing of high temperature (>450 °C) corrosion inhibitors and/or cladding is compulsory. A list of available cladding materials used in piping industry and in metallurgy are presented in Table 8.5. Some of them seem promising for use in superhot geothermal wells, but field testing is needed.

Metal alloy	Remarks	
Aluminium & its alloys	Pitting and stress corrosion cracking (SCC)	
Low carbon steel	Standard in present geothermal power plants; additional wall thickness is added to increase service life	l∎
Cast iron	Cannot resist mechanical & thermal sock	Icrea
Stainless steel	Needs oxygen to remain stainless; immune to: crevice <20 °C; pitting <35 °C; SCC <150 °C	sing cor
Nickel	H ₂ S immunity <65 °C; attached by metal chlorides	rosio
Copper, brass, bronze, and other copper alloys	H ₂ S attacks copper	n resist:
INCONEL	Crevice & pitting immunity <85 °C	ance
Silver	Expensive	in sea
Passivated stainless steel	Protective oxide layer will be eroded in oxygen free media; immune to pitting corrosion <78 °C	awater a
MONEL	Its copper is attacked by H ₂ S	It 25°
Hastelalloy C22	Immune to: pitting <102 °C; crevice <150 °C	Ő
Titanium	Immune to corrosion up to 300 °C	
Titanium grades 19 & 20	Recommended for geothermal brines	

Table 8.4: Ranking metals and their alloys in terms of corrosion resistance; Corrosion free operation with geothermal fluids above 300 °C cannot be guaranteed by even the most resistant alloys.

Pipe lining	Remarks	
Organic, Epoxy	Max service $T < 60-90^{\circ}C$	
Cement mortar	Max service T < 100°C	
Glass lining	Max service $T < 250^{\circ}C$	
Zirconium Alumina Ceramic	Limited corrosion resistance	
Cast Basalt	Max service T < 450° C; Thermal shock resistance up to Δ T=150°C almost absolutely acid/alkali resistant	
Alumina Ceramics	Max service T < 1700°C Limited corrosion resistance	
Nitride or Reaction Bonded Silicon Carbide	Max service T < 1500°C Limited corrosion resistance	
Aluminium-zircon-silicate cast	Max service T < 1000°C Thermal shock resistance up to Δ T=950°C High chemical resistance	
Sintered Silicon Carbide	Max service T < 1750°C Outstanding corrosion resistance	

 Table 8.5: Available pipe lining materials from piping and metallurgical industries; internal wall pipe linings that seem promising for ultra-hot geothermal fluids are cast basalt, cast aluminium-zircon-silicate and sintered silicon carbide.

8.4 Recommendations

As the ultimate goal is to achieve reliable electricity generation from stand-alone superhot geothermal wells, key challenges for the new superhot well are to demonstrate reliable long term fluid treatment and steam purification methods and surface equipment. Suggested field experiments and tests should include optimizing wet scrubbing method for higher conversion efficiency, downhole wet scrubbing, dry scrubbing, as well as testing new corrosion resistant materials and equipment for operation at extreme temperatures & pressures.

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9 Attachments

Safety data sheets of chemical substances mentioned in chapter 5 on high temperature tracers follow:

SIGMA-ALDRICH

sigma-aldrich.com

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006 Version 6.0 Revision Date 03.05.2017 Print Date 05.10.2018 GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1	Product identifiers Product name	:	Ammonium perrhenate	
	Product Number Brand REACH No.		316954 Aldrich A registration number is not available for this substance as the substance or its uses are exempted from registration, the annual tonnage does not require a registration or the registration is envisaged for a later registration deadline	
	CAS-No.	:	13598-65-7	
1.2 Relevant identified uses of the substance or mixture and uses advised a			e substance or mixture and uses advised against	
	Identified uses	:	Laboratory chemicals, Manufacture of substances	
1.3	Details of the supplier of the safety data sheet			
	Company	:	Sigma-Aldrich Norway AS Filipstad Brygge 1 N-0252 OSLO	
	Telephone Fax E-mail address	::	+47 23 176000 +47 23 176010 eurtechserv@sial.com	
1.4	Emergency telephone number			
	Emergency Phone #		+(47)-22591300 (Giftinformasjonen) +(47)-21930678 (CHEMTREC) Brann og større ulykker 110 Ambulanse medisinsk nødtelefon - 113	

SECTION 2: Hazards identification

2.1 Classification of the substance or mixture

Not a hazardous substance or mixture according to Regulation (EC) No. 1272/2008.

2.2 Label elements

2.3 Other hazards

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher. Lachrymator.

SECTION 3: Composition/information on ingredients

3.1 Substances

Aldrich - 316954

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Formula	:	H ₄ NO ₄ Re
Molecular weight	:	268,24 g/mol
CAS-No.	:	13598-65-7
EC-No.	:	237-075-6

No components need to be disclosed according to the applicable regulations.

SECTION 4: First aid measures

4.1 Description of first aid measures

If inhaled

If breathed in, move person into fresh air. If not breathing, give artificial respiration.

In case of skin contact Wash off with soap and plenty of water.

In case of eye contact Flush eyes with water as a precaution.

If swallowed

Never give anything by mouth to an unconscious person. Rinse mouth with water.

- 4.2 Most important symptoms and effects, both acute and delayed The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11
- 4.3 Indication of any immediate medical attention and special treatment needed No data available

SECTION 5: Firefighting measures

5.1 Extinguishing media

Suitable extinguishing media Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

- 5.2 Special hazards arising from the substance or mixture No data available
- 5.3 Advice for firefighters Wear self-contained breathing apparatus for firefighting if necessary.
- 5.4 Further information No data available

SECTION 6: Accidental release measures

- 6.1 Personal precautions, protective equipment and emergency procedures Avoid dust formation. Avoid breathing vapours, mist or gas. For personal protection see section 8.
- 6.2 Environmental precautions No special environmental precautions required.
- 6.3 Methods and materials for containment and cleaning up Sweep up and shovel. Keep in suitable, closed containers for disposal.
- 6.4 Reference to other sections For disposal see section 13.

SECTION 7: Handling and storage

7.1 Precautions for safe handling Provide appropriate exhaust ventilation at places where dust is formed.

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For precautions see section 2.2.

7.2 Conditions for safe storage, including any incompatibilities

Keep container tightly closed in a dry and well-ventilated place. Store in cool place.

7.3 Specific end use(s) Apart from the uses mentioned in section 1.2 no other specific uses are stipulated

SECTION 8: Exposure controls/personal protection

8.1 Control parameters

Components with workplace control parameters

8.2 Exposure controls

Appropriate engineering controls General industrial hygiene practice.

Personal protective equipment

Eye/face protection

Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin protection

Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and the standard EN 374 derived from it.

Body Protection

Choose body protection in relation to its type, to the concentration and amount of dangerous substances, and to the specific work-place., The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection

Respiratory protection is not required. Where protection from nuisance levels of dusts are desired, use type N95 (US) or type P1 (EN 143) dust masks. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Control of environmental exposure

No special environmental precautions required.

SECTION 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

a)	Appearance	Form: crystalline Colour: white
b)	Odour	No data available
c)	Odour Threshold	No data available
d)	pH	No data available
e)	Melting point/freezing point	313 - 314 °C - Decomposition
f)	Initial boiling point and boiling range	No data available
g)	Flash point	Not applicable
h)	Evaporation rate	No data available
i)	Flammability (solid, gas)	No data available

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	j)	Upper/lower flammability or explosive limits	No data available
	k)	Vapour pressure	No data available
	I)	Vapour density	No data available
	m)	Relative density	3,97 g/mL at 25 °C
	n)	Water solubility	62,3 g/l at 20 °C - completely soluble
	0)	Partition coefficient: n- octanol/water	No data available
	p)	Auto-ignition temperature	not auto-flammable
	q)	Decomposition temperature	No data available
	r)	Viscosity	No data available
	s)	Explosive properties	No data available
	t)	Oxidizing properties	The substance or mixture is not classified as oxidizing.
Other safety information			
		Bulk density	2.132 ka/m3

SECTION 10: Stability and reactivity

10.1 Reactivity No data available

9.2

- 10.2 Chemical stability Stable under recommended storage conditions.
- 10.3 Possibility of hazardous reactions No data available
- 10.4 Conditions to avoid No data available
- 10.5 Incompatible materials Strong reducing agents, Strong acids

10.6 Hazardous decomposition products Hazardous decomposition products formed under fire conditions. - Nitrogen oxides (NOx), rhenium oxides Other decomposition products - No data available In the event of fire: see section 5

SECTION 11: Toxicological information

11.1 Information on toxicological effects

Acute toxicity

LD50 Oral - Rat - male and female - > 2.000 mg/kg

Skin corrosion/irritation Skin - Rabbit Result: No skin irritation

Serious eye damage/eye irritation

Eyes - Rabbit Result: No eye irritation (OECD Test Guideline 405)

Respiratory or skin sensitisation

- Mouse Aldrich - 316954

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Result: Not a skin sensitizer. (OECD Test Guideline 429)

Germ cell mutagenicity

reverse mutation assay Salmonella typhimurium Result: negative

Micronucleus test Human lymphocytes Result: negative

In vitro mammalian cell gene mutation test mouse lymphoma cells Result: negative

Carcinogenicity

No data available

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

Reproductive toxicity

Specific target organ toxicity - single exposure No data available

Specific target organ toxicity - repeated exposure No data available

Aspiration hazard No data available

Additional Information

Repeated dose toxicity - No data available(Ammonium perrhenate) RTECS: Not available

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

SECTION 12: Ecological information

12.1 Toxicity

Toxicity to fish	static test LC50 - Danio rerio (zebra fish) - > 100 mg/l - 96 h (OECD Test Guideline 203)
Toxicity to daphnia and other aquatic invertebrates	static test EC50 - Daphnia magna (Water flea) - > 100 mg/l - 48 h (OECD Test Guideline 202)
Toxicity to algae	static test EC50 - Desmodesmus subspicatus (Scenedesmus subspicatus) - 139,6 mg/l - 72 h (OECD Test Guideline 201)
Toxicity to bacteria	EC50 - activated sludge - > 1.000 mg/l - 3 h (OECD Test Guideline 209)

- 12.2 Persistence and degradability No data available
- 12.3 Bioaccumulative potential No data available

12.4 Mobility in soil No data available

12.5 Results of PBT and vPvB assessment

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This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

12.6 Other adverse effects

No data available

SECTION 13: Disposal considerations

13.1 Waste treatment methods

Product

Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging

Dispose of as unused product.

SECTION 14: Transport information						
14.1	UN number ADR/RID: -		IMDG: -		IATA: -	
14.2	UN proper ADR/RID: IMDG: IATA:	shipping name Not dangerous goods Not dangerous goods Not dangerous goods				
14.3	Transport ADR/RID:	hazard class(es) -	IMDG: -		IATA: -	
14.4	Packaging ADR/RID:	group	IMDG: -		IATA: -	
14.5	Environme ADR/RID: n	ntal hazards	IMDG Marine pollutant:	no	IATA: no	
14.6	Special pre No data ava	ecautions for user ailable				

SECTION 15: Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture This safety datasheet complies with the requirements of Regulation (EC) No. 1907/2006.

15.2 Chemical safety assessment For this product a chemical safety assessment was not carried out

SECTION 16: Other information

Further information

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The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.sigma-aldrich.com and/or the reverse side of invoice or packing slip for additional terms and conditions of sale.

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