SCIENTIFIC INVESTIGATIONS AND TECHNOLOGICAL DEVELOPMENT IN THE LARDERELLO REGION FROM XVI THROUGH XIX CENTURIES

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ABSTRACT

After an introduction of a general nature, purported to provide the subject in question with a brief historical framework on the geothermal knowledge accumulated in the Mediterranean area up until the end of the Middle Ages, the paper summarizes the investigations made and the ideas expressed. as well as the main technological innovations achieved at Larderello from the heginning of the Renaissance until the end of the last century.

The description of the natural manifestations, the hypotheses made on their formation and evolution in time. and the theories proposed by numerous authors on the formation of the Larderello field and an the nature of the hydrothermal products. altogether constitute a set of very stimulating ideas. These indicate that the understanding of the geothermal phenomena and the technological development achieved at Larderello had already reached. by the beginning of the present century, a high level of scientific and applied importance.

1. INTRODUCTION AND HISTORICAL BACKGROUND

The description of the principle natural manifestations and the formulation of the first explicative hypotheses on their presence in various localities of the Mediterranean area date hack to many centuries before the Christian era. From then onwards throughout Antiquity, the presence of hot springs and the occurrence of many manifestations directly or indirectly controlled by the terrestrial heat (fumaroles, active volcanoes, hydruthermal mineralizations. eanhquakes, etc.) called the attention of numerous Greek and Latin writers, who dealt with them in poetic-allegorical terms and/or in scientific-philosophical terms in the light of the naturalistic and cosmogonical theories of their time (Cataldi - Chiellini, 1995: this Volume). It thus came to form by progressive accretion. throughout the nearly thousand years period preceding the Middle Ages, a first hut very imponant nucleus of scientific knowledge on the geothermal phenomena and on the modalities in which terrestrial heat manifests itself at the surface. This first nucleus constituted the basis for the more advanced development of the scientific understanding of geothermal energy. which was to take place from the first centuries of the second millennium onwards.

In reality. the use of natural heat for balneotherapy. and the exploitation of hydrothermal products for a wide range of practical applications. had reached in Antiquity its boom in the period of maximum splendor of the Roman Empire (III century A.D.): bur all these uses underwent a fast decline from the VI century A.D. onwards, following the Fall of Rome. The utilization of eanh energy and hydrothermal products then fell into a lung period of lethargy which lasted up until after the beginning of the second millennium.

Attempts to describe or speculate on the origin of some geothermal phenomena also disappeared during this period. Therefore. there is a gap of some seven centuries. from the Fall of the Roman Empire until the middle of the XII century. during which almost no literature can he found with the description of geothermal phenomena or the direct use of terrestrial heat throughout the Mediterranean area.

An awakening of interest in the practical utilization of natural heat and hydrothermal products started to occur in the Mediterranean area during the first decades of the XII century. This awakening took place just in the area of Larderello whrre the existence of conspicuous hydmthermal deposits associated with the natural manifestations began to constitute, from the heginning of the XII century onwards, an objective of domination by the city states that were forming in Tuacany at the time (Burgassi, 1987; Cataldi *et al.*, 1992-'93).

Along with a renewed practical interest, starting from the same period a new literary flowering began to take place fur the manifestations in question. Numerous Italian and some foreign authors began in fact tu write about these manifestations from the XIII century onwards: some authors to make considerations of a religious nature, others to give a phenomenological and interpretative description, and still others to illustrate the therapeutic properties of the hot waters and hydrothermal muds of the area under discussion.

To mention all these authors would bring us outside the theme of this paper. We therefore refer the interested reader to the two papers cited above and to the bibliography contained therein. However. just to point out the importance of the evolution of the scientific knowledge of the Larderello field, we cannot fail to quote Ristoro d'Arezzo. In his work of 1282, this author described a huge explosive phenomenon which took place in a *lagone* (i.e. a natural pool of boiling water: plural *lagoni*) situated to the south of the area under discussion. His detailed description leads us to think that the phenomenon in question was a "phreatic explosion"

This introduction has no intention to deal (yet concisely) with the scientific contribution given to the understanding of geothermal energy by many authors of the Antiquity and of the first five centuries of this millennium. It has the only scope of supplying the readers of this paper wilt a brief picture of the historical hackground of grothermal energy in the period preceding that under examination, and therefore serves only to underline how the development of the geothermal knowledge of the area in question takes its roots in the antiquity of history.

2. XVI AND XVII CENTURIES

The first important author who at the heginning of the XVI century dealt systematically with the natural manifestations and the hydrothermal products of the Larderellu area was the German

naturalist and medical doctor Georg Bauer (1494-1555). He is better known as **Georgius Agricola**, the "father of mineralogy".

The description and the scientific explanation of the manifestations of Larderello and of the hydrothermal minerals associated with them was made by Agricola following a method of comparative analysis with similar manifestations of other Italian geothermal areas. The results of this analysis appear in three works: *"De re metallica"* (published posthumously in 1556), *"De veteribus et novis metallis"* (1546) and *"De natura eorum quae effluent ex terra"* (1546). This latter work describes the characteristics of geothermal fluids.

More or less contemporary with the above mentioned works is the treatise *"De balneis omnia quae extant apud graecos, latinos et arabos"* (Giunta Edit., 1553). It is made up by a series of specific monographies, each of which deals with a major geothermal area of the Mediterranean region. In each of these monographies a description is given of the concerned geothermal site and of the therapeutic properties of the thermomineral muds and thermal waters to be found there. Among the monographies regarding the Larderello area, those of the following authors are to be noted: **Mengo Blanchello Faentino**, **G. Franciotti**, **M. Savonarola**, **Bartolomeus Taurinensis** and **Ugolino da Montecatini**.

The work of the naturalist **A. Baccio** (1571) follows shortly after. This author was concerned in particular with the genetic cause of the natural manifestations, and attributed their formation to the presence of a "subterranean fire". He also discussed the origin of the sulphureous incrustations associated with the manifestations of a fumarolic type.

Another author who, towards the mid XVI century, dealt with the natural manifestations and the hydrothermal products of the area in question was **U. Aldrovandi** (1522-1605). In particular, this author described the presence, among these products, of a mineral which he called *nitrum nativum*. From the description given and from successive sources (M. Mercati, 1717; U. F. Hoefer, 1777) we understand now that this mineral was the boric acid.

Towards the beginning of the XVII century, the anatomist and medical doctor **G. Falloppio**, in an important work published in 1606, described the characteristics of the manifestations of Larderello, paying particular attention to the therapeutic properties of the different thermal waters for the cure of various illnesses. Concerning the genetic causes of the manifestations, he restated the concept of Baccio and attributed their formation to the presence of a "subterranean fire".

A little later, the German geographer Phillip Clüver (1580 - 1622), better known as **Cluverius**, the "founder of historical geography", made a detailed description and prepared the first geographic map of the Larderello region, with the location of all main natural manifestations. The work including this map was published posthumously in 1624.

In the second half of the XVII century, the Larderello region attracted the attention of the Danish physician and geologist Nils Steensen, better known by his Latin name **Nicolaus Steno** (1638 - 1686). During his stay in Florence as physician of the Grand Duke Ferdinand II this author studied the geological characteristics of many Tuscan areas. Among these areas, the Larderello region was described in much detail because of its geological peculiarities. In his work *"De solido intra solidum naturaliter contento dissertationis prodromus"*, published in 1669, among other things, this author recognized the nature of volcanoes and mantained that the natural manifestations of Larderello represent "exhalations" of a criptovolcanic activity.

3. XVIII CENTURY

Towards the beginning of the XVIII century, the already mentioned **M. Mercati**, Italian mineralogist, started to study systematically the hydrothermal deposits associated with the natural manifestations of the Larderello region. During his study, the results of which were published in 1717, Mercati recognized the presence and made the description of several hydrothermal minerals, including that which he called *nitrum volaterranum*. Based on the description given (*"nitrum nativum scissile ex quo venetis borax conflatur"*, which means "the native nitrum from the processing of which Venetians obtain the borax"), and from successive sources (U. F. Hoefer, 1777), it is possible now to say that this mineral was the boric acid.

A few decades later, the Italian scientist **G. Targioni Tozzetti** was appointed by the Granduke of Tuscany to evaluate the potential development of the agricultural and mineral resources of the Granduchy. Thus, in 1742 he began a series of detailed field surveys in numerous areas, which lasted approximately 25 years. The results of all these surveys were published in 1769.

As regards the geothermal resources, the author did not limit himself to a simple description of the natural manifestations and *lagoni* (Fig. 1), and to a mere listing of the hydrothermal minerals amenable for cultivation and commercialization (alum, *nitrum volaterranum*, sulphur, *vitriol* i.e. hydrated ferrous sulphate, etc.); he also endeavored to discuss critically the geothermal phenomena of Larderello in the light of the theories proposed up to his time.

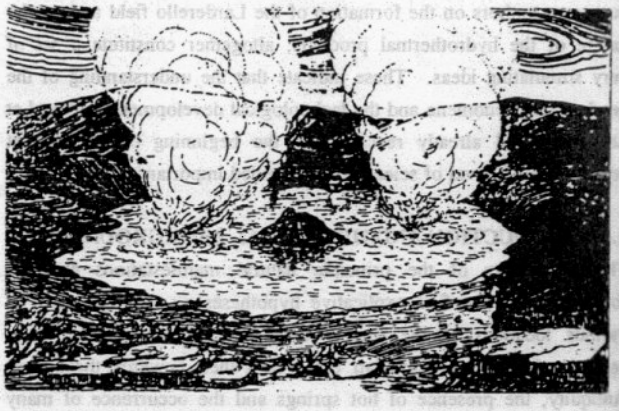

Figure 1: Sketch of a *lagone* (from A. Targioni Tozzetti, 1769).

Regarding the natural manifestations and the *lagoni* of the region, Targioni Tozzetti wrote textually:

".... In all of them, I have identified alum, salt, sulphur and vitriol. Baccio says that a "subterranean fire" (exists and) is the cause of heat and boiling; however, if he means "real fire", as in the case with volcanoes, he his wrong, simply because there is no fire escaping (from those manifestations). At most, there is a continuous hot fermentation, like certain fermentations that occur chemically with two or more cold liquids.....

.....Not only the *lagoni*, but all the mineral waters and mofettes I have observed, spring out from fractures of primordial mountains, but never from hilly terrains. This means that the minerals formed within mountain ridges. As time passed, some small portions of the veins in which the inflammable material was trapped, came to outcrop; therefore, this material could come into contact with outside air and a small amount of (surface) water started to percolate into the veins. This water may be sufficient to trigger off the fermentation process, drive out the air trapped within fractures, release heat and cause the water to boil. For sure, large masses of inflammable material are scatteredly present within rock mountains, much larger than we might suppose, and one day in the future (this material) will come to

outcrop and start to ignite(by fermentation).....

..... In other lagoni....., deep. round-shaped holes are to be seen. like those made by the tarantula; from this type of holes. nothing but very hot air blows out. (In this case), if you hold a silver coin against the air stream, a veil of condensation forms, much as it happens if you breathe on a mirror. It is an extremely line coal of water. trasteless but sulphur-smelling; in less than a minute, the coin turns black. as if it were made of iron. On the upper surface of many of them holes a substance similar to pumice is deposited. I doubt very much. however. if this substance is that which Aldrovandi cells *"alumen volaterranum...., facultatis astringentis...."* (i.e. alum from Volterra...., with astringent properties. ...).

Targioni Tozzetti even recognized the effects of self-sealing; however, he could not understand fully the causes of this phenomenon. In this regard. hc wrote:

".... The *lagoni* continually undergo an expansion process, and tend to move towards the mountain top. (Cultivation) fields which until a few years ago were richly fertile. now yield nolhing, because they have been crossed by the tortuous fissures created by the spreading *lagoni*. This expansion and encroachment on Once fertile fields indicate that this type of *lagoni* eventually reach and settle in correspondence to large veins of the original (inflammable) material. and this (shifting process) continues until the whole (original) materialhas been consumed. However. there is not doubt that the expansion (of the *lagoni*) is a process which becomes weaker day by day, and that in certain places it lias halted since a long lime. The many dried. up and (now) cold. round-shaped lacustrine depressions, wliich can be seen here and there in the valleys (of the **Larderello area).** are evidences of this (extinguished **process).** There (depressions) appear (now) as extremely barren places and look like craters, the bottom of which is filled with collapsed blocks of *alberese* (i.e. a type of marly limestone); thus, these (craters) are to be considered (old *lagoni)* similar to the presently active lagoni, the only difference being the fact that no s t e m is released (from the former)'.

A few years after the conclusion of the geological study by 'Targioni Tozzetti, a very important scientific result was achieved in 1777 by U. F. Hoefer (the chief chemist of the pharmacies of the Gran Duke of Tuscany), who documented analytically the presence of boric acid in the water of two *lagoni* of tlie Larderello area, located near Monterotondo and Castelnuovo.

As a matter of fact. the boric acid (then known as "Homberg's sedative salt"). though present among the hydromineral products associated with the natural manifestations, had not yet been recognized as such and separated chemically: therelore. the confirmation of its presence at Larderello and the success of the Hoefer's chemical separation process opened the path for the take off of a flourishing geothermal industry in the region.

As boric acid (a substance widely used in pharmaceutical industly) was in that period obtained from minerals imported by land from distant Persia. the discovery made lhy Hoefer immediatly resulted in plans for its industrial production at Larderello by exploiting the boric compounds associated with tlie geothermal manifestations.

Thus, with the support of the Granduke of Tuscany, two complementry groups of activity were soon started at Larderello: *i)* one of a practical nature, directed at drilling for hot fluids (to be used for extraction of horic acid, as well as a primary energy source to drive mechanical engines). and *ii)* the other of the scientific nature, directed at improving the knowledge of the geothermal phenomena.

In this regard. the scientific and technological contribution given hy P. Mascagni (professor of chemistry, physiology and anatomy at several Tuscan Universities) must be recognized. In an important work published in 1779, he made a detailed mineralogical description of the hydrothermal products to be found in the Larderello region, and maintained in particular that certain "white concretions" which Targioni Tozzetti had thougth to he selenite were in fact boric acid.

In tlie following years Mascagni faced the problem of how tu exploit large quantities of bori· acid for industrial production. and proposed that natural heat rather than wood fire could be used to evaporate boric brines. Thus, he designed two differing types of metal boiler. one to be enbedded into lhot grounds on Le top of natural manifestations. and the other to be partially sunk into the *lagoni*.

4. XIX CENTURY

For a number of reasons, the new technology proposed by Mascagni could not take root immediately at Larderellu. However. another technologist, G. Guerrazzi, at the beginning of the XIX century, took up the ideas of Mascagni. After having developed a more advanced model of metal boiler, he used it for a series of on site experiments. Thus. he could perfect a process for the production of boric acid. which enabled him not only obtaining very concentrated boric brines, hut also their drying and dehumidification. Furthermore, in a system of integrated use of the heat and of the saline content of the geothermal fluids, Guerrazzi also experimented wilh a new process for the production of borax starting from boric acid. The results of the experiments and processes in question were published in his work of 1819.

Despite all this. for the commercial application of Mascagni's innovative ideas arid of Guerrazzi's equally innovative processes. it was necessary to wait some ten years more. until 1827. From that year. having understood that these ideas and processes could have great importance for the chemical industry, following a series of visits to the area which would take his name, F. Larderel (a French entrepreneur established in Tuscany) obtained from the Granduke of Turcany tlie lease tu exploit the boric minerals associated with some natural manifestations of the region. He then began to apply the technology proposed by Mascagni and developed by Guerrazzi.

Howeever, to obtain the "raw material'. F. Larderel did not limit himself to the simple exploitation of the saline incrustations deposited around tlie natural manifestations. In fact. from 1832 he also endeavored to obtain a greater quantity of "raw material" from primary geothermal fluids, by means of the manual drilling of shallow wells around the edge of the manifestations. The first wells did not. however, give the desired results. For this reason. Larderel was easily convinced to suspend this wurk by his technical adviser of the time, the French scientist A. Payen.

Furthermore, still with a view to obtaining larger quantities of "raw material", F. Larderel had large pits excavated in the areas of dried up natural pools (the so called *dried lagoni*); he thus created. by filling these pits with fresh water. a number of *artificial lagoni*.

Moreover, above each of the natural and artificial *lagoni*, F. Larderel had a brick dome built. at the top of which a riveted metal pipe was inserted to collect the steam accumulated inside the dome (Fig. 2). This construction, which was named *lagone coperto* (i.e. "covered lagoon"), enabled channelling the steam collected at the tup of the brick domes towards evaporating tanks where boron-rich waters were channelled from the bare of each brick structure.

The "covered lagoon" represented a very important technological innovation. In fact. even though its basic concept was derived from the Mascagni's proposal and Guerrazzi's experiments. the "covered lagoon" and the associated equipment (collection pipes. boiler and evaporation tanks) constitued as a whole a low-pressure separator coupled with a heat exchanger.

In the meantime, there was a growing scientific interest in Le geothermal phenomena of the area under discussion. with various

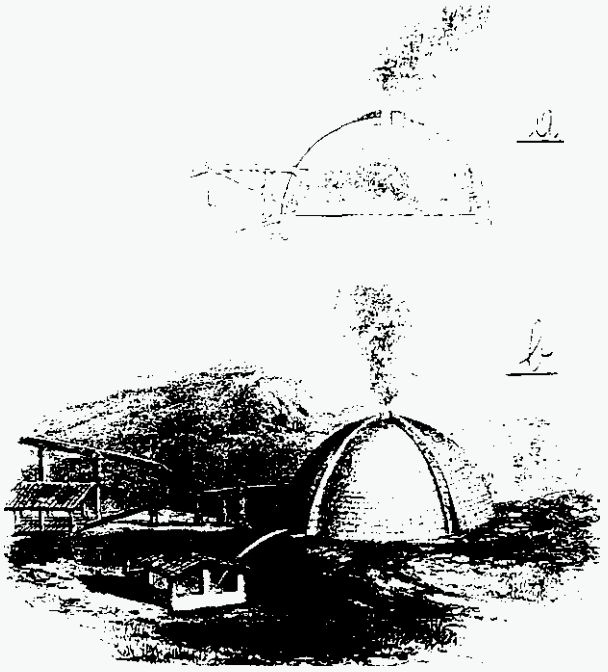

Figure 2: **"Covered lagoon" (from an old print of 1821).**
a) Cross section; b) Prospect view.

types **of** scientific investigation: geological, mineral and chemical.

The Frenchman A. **Dumbs** (1828) stated that boric acid reaching the surface is the **result** of interaction between meteoric water and deep-**routed** large masses of hydmthermal minerals. among which boric acid and sulphur were present. **In** this way he also explained the occurrence of H_2S in the gas escaping from the *lagoni* and **steam** jets.

Two important geological works were puhlished in 1833 and 1863 hy P. **Savi.** professor of natural sciences at **Pisa** University. These works describe not only the rock formations of the Larderello region **and** surrounding areas, but also analyze the caracteristics of the solfataras and *lagoni.* and speculate on **the** hydrothermal circulation causing in places the alteration of outcropping **terrains.** Moreover. Savi recognized the existence of folding **and** faulting structures in the whole mountainous-hilly range known as the "metalliferous chain" (a sector of which is represented by the Larderello region). **and** maintained that a number of anticlines had been formed as the result **of the** emplacement. at relatively shallow depth. of intrusive bodies. The existence of these shallow intrusions could he inferred. according to the author. from **outcrops** of trachytes and selagites which are to be found in **several areas** of central and southern Tuscany.

In **the** years immediately successive to 1832. **the** proposals and experiments to develop a suitable drilling technology. specific to the conditions of **the** Larderello **area,** were intensified. While due to the limited space available fur this paper. it is impossible to mention all the fertile ideas advanced. and the many **experiments** made in the sector of drilling technology in the period between 1830 and 1870 (the interested reader. however, is referred to **the** paper by Burgassi, 1987). **note** must he made of the great innovative contribution given in this sector by the scientist **G. Gazzeri** (1838 and 1841).

This author came tu dedicate his effon to the development of drilling methods **after** having studied the geological situation and the depositional characteristics of the hydrotermal minerals **of** the area. As **concerns** horic acid, in particular, he had reached the conviction that the carrier fluids of this mineral were originally contained in a deep. single **and** huge reservoir. and that the natural manifestations were nothing but the **result** of local discharges of deep fluids. In this regard Gazzeri wrote textually:

'...The most elementary **notions of** geology **persuade us** that the mineral, whore decomposition gives off the boric acid contained in the ardent **vapour** of the **steam** jets. is **not distributed** in **isolated masses at** the **bare of** each steam **jet** or *lagone,* but forms **a** single and huge deposit. the **extension** of which **is** unknown (tu us). If we **were** able **to** reach the deposit by means of drilling. **a** spontaneous blow **out** should follow of natural fluids. similar **to** that occurring in artesian wells. Alternatively (if the spontaneous blow out does not **occur),** we could obtain **a** stimulated production (of the well) by a judicious injection **of** (fresh) **water** or by other methods...".

Consequent to these ideas the engineer **V. Manteri** (1841) conceived and constructed a new drilling equipment that could he enployed without tlie aid of **tlic** winch, and that enabled drilling holes about 10 cm io diameter.

In this same period the already mentioned A. **Payen** began to study the **decrease in** temperature and flow rate which started to be noted in some *lagoni* and steam jets located nearby the manifestations under exploitation: decrease that was **clearly related** to the extraction activity. Therefore, with **a** view to attenuating the above raid decrease, and **also** to obtaining a more efficient extraction cycle **of** the horic acid, Payen developed in 1841 **an** ingenious **system of** connection in cascade of the artificial *lagoni* (Fig.3).

The **Tuscan** region was **also** studied by the geologist **L. Pilla** who in 1845 maintained that the high-temperature heat is responsible in **certain areas** for the formation of **coal** and **natural** manifestations. In this regard he wrote:

".....Where partial outlets of igneous rocks **occur. the** vegetable material which transforms itself into lignite seems elsewhere. (in places) is baked into **lithantrax** because **of** the **exceptionally** high temperalure underground. **(On** the **other** hand). the famous *lagoni* in **Tuscany** can be considered the legacy **of** there underground conditions. One of the characteristics **of** there (*lagoni*) is **(in fact)** a very high temperature **of** Ihe terrains around (them).....".

Moreover. Pilla wan the first author who maintained that the steam jets of the Larderello area **are** the result **of** a regional **thermal** anomaly caused by the emplacement underground of granitic bodies and by the effusion of porphyritic and trachytic rocks. In fact. he **wrote:**

".....The **tourmaline** found in **granitic** and porphyritic **formations** outcropping in Ihe region, indicates that the steam jets are related **to** these (formations). **(Moreover),** it is a well-known fact that boric acid **is** a **component** of the tourmaline. This clearly points to a connection between the presence **of** boric acid in the Steam jets and the formations said above.....".

The geological peculiarities **of** the manifestations and **the** fame which Larderello gradually acquired hecause of the production of boric acid. called also. in that same period. the attention of some foreign scientists. Among these **we** should mention the Englishmen W. **Hamilton, R. Murchison** and **R.** Warington. whose original works **were** puhlished in 1844. 1850 **and** 1854, respectively.

In 1851 the work of Murchison was translated into Italian hy **P.** Savi (already mentioned) and G. **Meneghini,** professors from Pisa University, who were also studying in that period the geology of Larderello.

In an appendix to the work of Murchison there authors, among other considerations. made the following comment:

"...As concerns the numerous steam jets. it should be noted that they seem to spring out from fissures running along NW-SE trends.... There regular. parallel. eruptive fissures are clearly the rejuvenation of older fissures which had been formed in preceeding eras as **a** result **of** violent underground **movements** caused by the high temperature regime....." (Fig. 4).

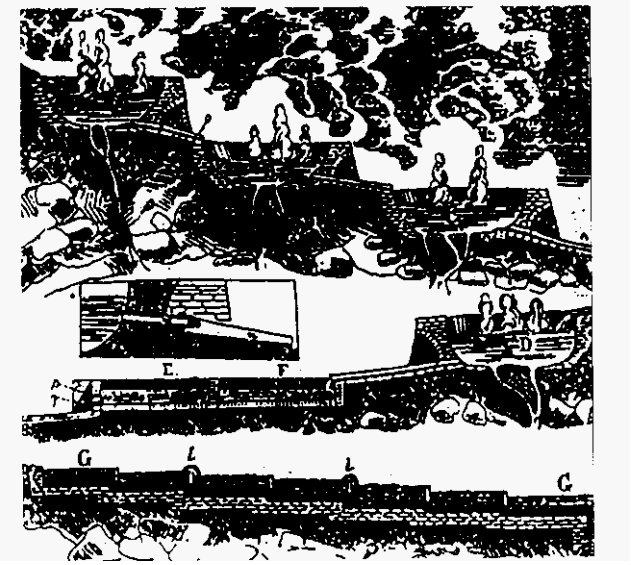

Figure 3: Old print showing a system of *lagoni* in cascade **(from** A. **Payen, 1841).**

Soon after the publication in Italy of the translation **version** of his **first paper.** Murchison visited the Larderello **region** and concluded that the steam jets **were** not a "phenomenon apan": rather, in the framework of the regional geological structure of Tuscany. **they** had to **he** considered late manifestations of the same volcanic process which **in** the **past** had affected **several areas** of central Italy. Moreover, **in agreement** with Savi and Meneghini, he pointed out that the steam jets and other natural manifestations were to he found along NNW-SSE alignements, which correspond to the main tectonic **trend not only** of Tuscany but of the whole Italian peninsula.

Others authors, such as **C. Deville** from **France** (1857) and **R. Wagner** from Britain (1875). maintained that boric acid was the result of interaction between hot wafer **and** deep-routed **masses** of boron azides. In this way, **they** justified **the presence** of ammonia in the waters of the *lagoni* and thermal springs.

On tlie other hand. the already mentioned Meneghini published in 1867 a specific paper on **the** production of boric acid. In this work. he made new observations on the depositional charecteristics of the hydrothermal minerals. discussing their formation in the light of the ideas of the time **on** the magmatic origin of the geothermal **fluids.**

Meneghini's **paper** proved to **he** a fundamental **reference** to the naturalist and **geographer** A. **Stoppani** who, in a notable work published **in** 1874. dedicated ample space to tlie phenomena of Larderellu. In this work. Stoppani look up various geological **and** phenomenological **ideas** already **advanced** by other authors (tectonic control of the alignments of manifestations, migration **in time of** the steam jets, thennal anomalies determined **hy** igneous processes, etc..), but he developed them in the geological framework of the whole Tuscany. adding also **some** new ideas of his own. In particular, not only **did** he **understand** well the mechanism which controls the occurrence of "phreatic explosions", **hut also the** cause of the phenomenon now **known as** "self sealing". Follows **an** original **passage** of the Stoppani's work **on these aspects:**

"....As I have already pointed out, the s t e m of the manifestations carries not only boric acid **but also other** compounds. as **for istance** ammonia. **sulphates,** iron. manganese. magnesia and **soda.** There (compounds) **crystallize** when the steam **cools,** and then they **incrustate** their subterranean passages. to the point **of** closing them completely. Boric acid. for istance, does **cause the** scaling of the **artificial** bore-holes and, during drilling. large masses (of hydrothermal mineralizations) **are** found. which prevent **the** steam to **rise** to the **surface.** There is nothing more natural than a steam **jet** to ***close by itself at*** home. without finding **an** outlet. **As a** consequence. the so closed steam jet gathers **all** its power before breaching its **prison walls** and springing out again **to the** surface like **an unshakled** prisoner who has just escaped. The **steam** jets sometimes **blow** out spontaneously. **just** like a bomb. The **soil** is (then) **tossed** into the air. and **a steam** cloud **blows** out: the steam is sometimes **accompained** by **a jet of** boiling **water** which recalls a geyser.....".

In the following years other Italian and foreign scientists speculated on the origin of the boric acid.

I,. Dieulafait from **France** (1877) proposed that **boric** acid contained in the steam **jets resulted from** the leaching, by meteoric waters. of huried evaporitic sediments of Miocene age. In particular. he stated **that heat anomaly** is certainly attributable to **magmatic masses.** whereas the steam is the result of a vapourization process of meteoric **waters** percolating through fissures into high-temperature deep **formations.**

G. **Stohaman** and **P. Schwarzerberg** from **Germany** (1888) supported tlie **Dieulafait's** theory, hut tlie Italian mineralogist **G. D'Achiardi** (1878) **did** nut. This author. **in** fact, maintained that the steam escaping from natural manifestations originates within rock formations which are much **older** than the Miocene evaporitic sediments, underlie the latter **and** have no intercalated saline **layers.**

E. Bechi (1891), however. taking **into** account that **serpentine rocks** widely outcrop and have thickness of **inany** hundreds **meters** in the Larderello **region,** made the **hypothesis** that boric acid originates **by** the decomposition of the boron silicates contained in **these** rocks: decomposition caused by CO_2 streams rising **from** deeper formations.

The outstanding Italian geologist **C. De Stefani,** too. opposed strongly Dieulafait's theory **on** the origin of boric acid from Miocenic evaporitic **sediments.** and stated that this compound could **not** form hut at great depth After having studied tlie **lithostratigraphic sequence and** the geological setting of all geothermal **areas** of **Tuscany, as** well **as** the **hydrogeological** conditions and the hydrothermal species **occuring** in all active and fossil manifestations present **in there** areas, De Stefani. in fact, wrote **in** 1897:

"...The considerable **surface** area **of** the **territory** where these (manifestations) **occur,** the fact that **natural** Steam carries boric acid everywhere it escapes (into the atmosphere). Ihe **presence** of other acids and gases. the high temperature and energy of the s t e m are **all facts** proving that both the steam and the **(boric)** acid originate at **(great)** depth. and thal they have nothing to do with shallow sediments and (Miocenic) saline **deposits.** (On **the** other hand)...., it is widely accepted thal temperature **increases with** depth (by ~ 3" C/100m) on the average: thus.

Figure 4: Old print showing an alignement of steam jets along a fault scarp in the southern sector of the Larderello region, as they could be seen in 1818.

steam with a temperature of 175° C comes from a depth of - 5 km....
... The (geothermal) waters have nothing to do with marine water.....: therelore. they should be of atmospheric origin, and percolate underground through the numerous (rock) cavities until they reach the deepest recesses of the earth....
...The presence of boric acid in the steam jets can only be justified if one accepts that its origin is in the depth of the earth. and that the steam jets are the last legacy of a volcanic activity. (As a matter of fact). this (activity) occurred in Tuscany Until not so long ago, and even today the final signs of such activity are quite evident. The steam jets do also carry carbonic acid and. as Steam rises from underground. it comes into contact with very old borate-bearing rocks: thus. boric acid is drawn from the ensuing decomposition (of the borates).... The volcanic origin of the boric acid contained in the (water of) *lagoni* is indirectly confirmed by the fact that the same compound is contained in the steam plumes of active volcanoes and solfatara craters. They too. just like the *lagoni*, bear witness to the presence of ammoniacal substances, sulphurous gases and carbonic acid....".

At the Same time. throughout the second half of the XIX century, parallel with the geological research and studies an the origin of boric acid, laboratory analyses of hydrothermal minerals from Larderello were undertaken. In addition to the confirmation of the occurrence of minerals already described (alum. boric acid. sulphur. etc..), the presence of previously unknown borates and sulphates was discovered: the *larderellite* and the *cerbolite*.
The first of these minerals. discovered in 1854 by the already mentioned Bechi. was initially described by the formula $(NH_4)_2 B_8 O_{13} \cdot 4H_2O$; but this formula was subsequently perfected by D'Achiardi and established as $(NH_4)_2 B_{10} O_{16} \cdot 5H_2O$.
The second new mineral was recognised by O. Popp from Britain in 1872. It was described by the formula $(NH_4)_2 SO_4 MgSO_4 \cdot 6H_2O$.
In successive years (1934). the same D'Achiardi had then to discover a third new mineral: the *ginorite* ($Ca_2 B_{14} O_{23} \cdot 8H_2O$).
Furthermore, the famous Italian chemist R. Nasini in 1895 began the systematic Study of gases contained in the steam or dissolved in the hot waters of geothermal manifestations and wells. Thus, he came to discover the presence of helium and argon gases at Larderello.

From the technological point of view, it should be recalled that. after the adoption of the F. Larderel's "covered lagoon" and of the Payen's system of artificial *lagoni* connected in cascade. another important step ahead was made in 1845 by the introduction of the so-called *caldaia adriana* (adrian boiler). This boiler, designed by the engineer A. Larderel (sun of F. Larderel), consists of a series of brick conduits internally lined with lead plates above which the boron-rich waters were circulated in counterflow tu the steam stream.
The equipment (which is to be considered a precursor of the modern counterflow heat exchangers) was refined in different steps between 1845 and 1890; this enabled to improve progressively the whole processing cycle of the boric acid: gathering of boric waters (produced by shallow drillings, or drained from simple or multiple *lagoni*), vaporization of brines. crystallization and drying of the horic minerals.

With the realization of the adrian boiler. the work of De Stefani and the initial research by Nasini, we could consider closed the XIX century and the period under consideration in this paper. All this period. and the XIX century in particular. was an extremely fertile period for scientific ideas. technological innovation and experiments. which resulted in the more advanced development of geothermal energy that would take place at Larderello in the present century. However. before closing this paper, we can not fail to remenber the contribution given to the knowledge of the Larderello field by some other Italian scientists who started their studies towards the end of the part century.

In 1904 E. Perrone took up again the hypotesis advanced by Pilla some fifty years earlier regarding the origin of boric acid and stated that Uiis mineral could not derive but from tourmaline decomposition. In fact, considering that in the years amund the end of XIX century the greater depth of drilling had enabled production of fluids with a temperamre above 200 °C, Perrone claimed that the original temperature of the primary steam could nut be lower than 250 °C. Thus, he concluded that the steam should come from depths of between 5 and 8 km, where the existence of tourmaline-bearing. still hot granitic masses could he inferred by Late Miocene - Pliocene granitic outcrops to he found in areas to the west of Larderello.
The already mentioned D'Achiardi, however. in a new paper puhlished in 1926. rejected the Perroni's theory and stated that, even though granitic masses were likely to exist at depth in correspondence to the area under exploitation, their tourmaline content would not suffice at all for the formation of the large qualities of boric acid produced at Larderello.
On the other hand, during the first decades of the present century. the already quoted Nasini did not limit himself to the study of geothermal gases, hut conducted a whole series of laboratory research and on site experiments of industrial production processes. 'The Nasini's wurk culminated in 1930 with the publication of a monograph which represented a bench mark for the geothermal literature until a few tens of years ago.
B. Lotti. an outstanding Italian geologist, conducted in-depth investigations in the Larderello region. He. too, opposed strongly the Pilla's and Perroni's theory on the origin of the boric acid. In this regard. he claimed that:
"..... Boron. fluorine and chlorine. along with superheated water constitute the most energetic dissolvents which contribute to the crystallization of eruptive rocks. (Therefore), it can be argued that boric acid is not derived from tourmaline-bearing granites. but that it had been formed before (the eruption of effusive rocks). Rather. the circulation at depth of boron rich waters. from one ride may have interacted with granitic magmas to the point that the formation of tourmaline was facilitated. and from the other side (the ascending branch of this circulation) can nourish (with boric acid) the steam jets and the fluid produced through drilling....."
From the structural point of view, Lotti recognized that the whole "metalliferous chain" of Tuscany (and therefore also the Larderello region) is characterized hy two different types of tectonic style: a plicative one, and a distensive one. Taking up the hypoteses made by the already mentioned Savi. but adding many new arguments. he attributed the first of these two styles to a prolonged phase of igneous activity, which would have begun in the Miocene with the intrusion in subsequent steps of granitic bodies (Elba, Giglio, Montecristo, Gavorrano and Campiglia), the age of which is progressively more recent from west to east. Such activity would then have evolved in time to become only of the effusive type in the Quaternary age. giving rise to the eruption of trachytic melts in a number of Tuscan localities (Capraia, Montecatini, Orciatico, Roccastrada and M. Amiata). The folding attitude of the positive features would thus represent. according tu the author, the result of the structural up-lift caused by the rising of igneous bodies: some intrusive. other extrusive bodies.
As regards in particular the Larderello field. taking into account the fact that no igneous rocks of any types outcrop in the area. Lotti argued that a granitic intrusion should exist at relatively shallow

depth. and should be rooted within a still active magma chamber. He then concluded that the magmatic body, while undergoing a cooling process, was to supply the Larderello geothermal system not only with heat, hut also with steam. In the framework of this theory, Lotti maintained that the steam released by Steam jets and other natural manifestations not only at Larderello but also at any other geothermal fields of the world (including geysers. solfataras, etc..) had to he regarded as the final stage of an active magmatic process.

This theory. which was perfected in different steps in the period 1900-1928, took the name of "Lotti's theory of juvenile origin of the geothermal fluids" and was accepted worldwide until about four dedades ago.

Finally, it is worth recalling that, during his thorough field surveys. Lotti compiled a detailed geological map of the Larderello area; it served as guideline for the field excursions during the *First International Geothermal* Congress, which was held at Larderello in 1928 in the framework of the 41th Congress of the Italian Geological Society.

5. CONCLUDING REMARKS

The development of scientific thought and the technological progress achieved at Larderello in the period between XVI and XIX centuries are outstanding indeed.

From the scientific point of view, the authors who dealt with the Larderello region in this period did nut limit themselves to a simple description of the manifestations and of the associated hydrothermal products. but they endeavored almost always to understand the origin of geothermal phenomena in the light of the geological framework in which the Same phenomena occur. Thus. a series of original explicative hypotheses were advanced in that period on numerous aspects of geothermal energy; hypotheses which, by successive refinements and elaboration. and by progressive accretion and integration. led to the formulation, towards the end of XIX - beginning of XX centuries, of the first organic theories on the formation of the Larderello field.

The principle subjects dealt with, and the new scientific concepts that took root in the period under discussion regard:

- the mineralogical characterization and the formation processes of the hydrotermal products:
- the structural control of the manifestations:
  the presence of a strong thermal anomaly and its cause (heat source determined by relatively young igneous processes: magmatic intrusions and/or volcanic activity):
- the formation of positive folding features and of rock fracturing due to granitic intrusions or magmatic extrusions;
  the percolation underground of meteoric water along fractures and/or through outcrops of permeable rock formations;
- the presence of reservoir rocks:
  the interaction at depth of meteoric water with reservoir rocks and hydrothermal minerals;
- the process of "self-sealing" and the phenomena of evolution in time of the natural manifestations;
- the circulation underground of meteoric water and its interaction with deep hot fluids;
  the origin of incondensable gases associated with geothermal steam and waters:
- the formation in places, at shallow depth, of hot fluid over-pressures capable of causing "phreatic explosions" and/or the formation of new Steam jets.

From the technological point of view. the innovations of the period in question were realized almost exclusively from the XVIII century onwards. The main ones regard the following sectors:

- gathering and separation of fluids from the natural manifestations ("covered lagoon" and artificial lagoons);
- connection of anificial lagoons in cascade:
- drilling technology (the so-called *verga artesiana*, four-legged rigs with and without winch. bits of various type. bailers to remove cuttings from the bottom of the wells. manual rotation of the drill stems, rigs with a 2-3 m high working floor, blow-out preventers, riveted metal casings, pipe joints. rotating jerky devices to ream the well walls. stimulation techniques by means of a flexible disk piston called serpent. etc.);
- evaporation, drying and processing of baric brines by means of hot natural fluids (boilers of differing type. counterflow heat exchangers, techniques to diversify and purify the different boric products. etc.);
  use of geothermal steam to drive pumps and mechanical engines.
  space heating (industrial and residential buildings. and green houses).

All these important technological innovations, the multiple use of geothermal heal and hydrothermal products. along with the equally as important scientific results obtained by numerous authvrs. clearly indicate that the understanding of the Larderello field and the practical developments achieved in the exploitation of its resources, had already achieved by the beginning of this century a level of great relevance.

All these achievements Constitute the basis for today's more advanced level of development of the earth's energy. not only at Larderello but also in numerous other geothermal fields throughout the world.

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