

DISTRIBUTION OF IMPURITIES AND GASES BETWEEN STEAM AND WATER PHASES OF THE GEOTHERMAL FLUID IN THE LOW PRESSURE ZONE.

K.O. Povarov¹

¹ *Scientific Training and Research Centre of Geothermal Energy of Moscow Power Engineering Institute
(Technical University), Moscow, Russia, 111250, Krasnokazarmennaya Str., 14, kpovarov@geotherm.ru.*

It is well known, that there is no uniform distribution of impurities and gases between steam and water phases of the geothermal fluid during the separation process in the fluid collection and distribution system of the geothermal power plant.

Also, it is known, that steam at thermal and nuclear power plants contains as much impurities and gases as it follows from the distribution coefficient $K_d = (C_{st}/C_w) = f(\rho_w/\rho_{st})$, where C_{st} and C_w – concentrations of the chemical compound in steam and water phases correspondingly, ρ_w/ρ_{st} – ratio of densities of water and steam phases. Ratio of concentrations of impurities and gases in steam and water phases depends on ratio of densities of these phases and have linear behavior in the logarithmic coordinates for the wide range of pressures, series of these rays which start from the critical point of water in P - V diagram was called – “Ray diagram”.

These dependences were discovered by Soviet scientists more than 55 years ago and then were proved by many experiments and tests. Domestic and foreign experiments were done in the wide range of pressure ($3 < P < 300$ bars), however during the whole of that time (more than 45 years) the survey pressure range very seldom went down lower than 70 bars and experiments with the geothermal fluid were newer done.

Our surveys show, that for the geothermal fluid (steam – water) the ratio $K_d = f(\rho_w/\rho_{st})$ has non-linear behavior for the whole series of impurities. This is a geothermal fluid characteristic, since it may contain up to 2000 of different chemical elements and compounds, impurities and gases with total concentration of those many times higher than in steam or feed water of thermal and nuclear power plants.

1. INTRODUCTION

Reliability and cost effectiveness of all power plants (PP) essentially depend on fluid (steam) quality and level of PP equipment operation, i.e. on strict following Technical Operational Regulations (TOR) including protection of equipment internal surfaces against forming of deposits upon metal surfaces and prevention of standby corrosion during forced closedown and stoppage (conservation of power equipment).

Table 1. Steam quality for different types of boilers

Critical index	Drum boilers with natural circulation with pressure, bars			Once-through boilers with pressure, bars	
	Up to 40	70 and More	140	SCP	OCP
Na^+ , ppb	60-100	15-25	5	< 10	5
SiO_2 , ppb	*	15-25	30-60	20	15
Conductivity, $\mu S m/cm$	*	< 0,5	< 0,3	< 0,5	< 0,3
pH	> 7.5	> 7.5	> 7.5	> 7.5'	> 7.5'

* - Standardized basing on operational experience; ' – At neutral-oxygen water-chemical regimes > 6,5 is permissible.

Experience of thermal power plants and especially nuclear power plants operation showed absolute necessity of keeping high quality of feed water and steam (Regulations 1996) and also

of strict control of non-exceeding maximum permissible concentration of corrosive-aggressive impurities and equipment corrosion products in them (see Table 1).

Quality norms for feed water and steam at power plants working with subcritical parameters are lower than those at nuclear and thermal plants with supercritical parameters unit.

Geothermal power plants are working in the zone of low steam pressures at turbine inlet ($P_0 < 20$ bar, normally $5 \div 10$ bars), so at the first approximation steam quality norms for drum boilers working at low steam pressures may be used as the norms for geothermal turbines.

Nevertheless, despite active development of geothermal energy in many countries round the world, there are still no general approved norms for quality of steam coming into geothermal turbines, and every geothermal turbine manufacturer establishes his own requirements towards steam quality upstream of turbine. Thus, for example (Geothermal Power 1995), Mitsubishi Heavy Industries company introduces quality norms for some geothermal steam elements (see Table 2) for its turbines during their normal operation, quotes the norms at which operation must be limited and norms at which turbine must be shut down immediately.

Table 2. Recommended quality norms for geothermal steam for MHI turbines

Operating regime/Impurities	Norma	Norm excess	Turbine shut down
<i>Total mineralization, mg/kg</i>	0,5	0,5 – 5	> 5
<i>Cl, ppb</i>	100	100 – 1000	> 5000
<i>SiO₂, ppb</i>	100	100 – 1000	> 5000
<i>Iron total, ppb</i>	100	100 – 1000	> 5000

It is known that geothermal fluid (superheated or wet steam, hot water under high pressure or steam-water mixture) may contain up to 2000 various volatile and nonvolatile impurities and gases. Geothermal fluid is an aggressive environment and causes intense corrosion and corrosive cracking of working blades metal and flowing part discs of geothermal turbines (Povarov *et al.* 2000). Therefore requirements to geothermal steam quality must be as strict as in traditional heat power engineering.

During process of the geothermal fluid moving along production well, in pipelines and equipment of fluid collection and disposal system, during separation process as well as steam expansion process in turbine redistribution of impurities between steam and liquid phases takes place, and as a result this causes formation of deposits and precipitation of corrosive-aggressive compounds upon power equipment internal surfaces that decrease its cost effectiveness and reliability during operation.

Therefore at modern GeoPPs, including Mutnovsky GeoPP, continuous chemical control (monitoring) of geothermal fluid is arranged (steam quality upstream of turbine, quality of steam condensate downstream of turbine, separated water, cooling water in the cooling towers) and also control of noncondensable gases contents in it. List of chemicals, control over which must be implemented during GeoPP operation, is given below.

Permanent control:—Steam quality: *Na, Cl, Fe, SiO₂, B, pH, and dryness*—Gases contents: *CO₂, H₂S, NH₃*

—Cooling water: *pH, Na, Cl, SO₄, NH₃, HCO₃, bacteria contents, turbidity***Periodical control:**

—Complete analysis of steam condensate and separate ion composition:

Li, Na, K, Ca, Mg, Cl, F, HCO₃, SO₄, B, SiO₂, As—Complete gas analysis:
CO₂, H₂S, NH₃, H₂, He, Ar, CH₄, N₂, Hg

Geothermal steam coming to GeoPP turbine is an evaporation product of geothermal water which is located in underground reservoir under high pressure and coming to surface by production well shaft into fluid collection and disposal system with its following division (separation) to steam and separate water in separators and flashers.

In all cases steam quality is defined by contents of impurities and gases which passed into steam during process of flashing and separation of geothermal fluid steam and water phases. At the same time transition of volatile and nonvolatile compounds takes place not only due to mechanical drip carryover but also due to natural dissolubility of these compounds in separators and flashers.

2. DISTRIBUTION OF IMPURITIES AND GASES BETWEEN STEAM AND WATER PHASES OF GEOTHERMAL FLUID

Profound analysis and calculations of steam quality at thermal and nuclear power plants are based on regularities of impurities and gases distribution stated by Soviet and other researchers. As long ago as in 1950s scientists of Moscow Power Engineering Institute (MPEI) and Central Boiler-Turbine Institute (CKTI) stated main linear regularities (Fig. 1) of distribution of a number of impurities between steam and water phases during change of phases pressure in the range $P_0 > 6 - 7$ MPa (Styrikovich *et al.* 1959). These researches permit today to determine reliably enough the chemical composition of steam upstream of turbines at thermal and even nuclear power plants.

Transition of boiling geothermal fluid admixtures into geothermal steam that is balanced with it or, on the contrary, transition of saturated steam admixtures into water (for example, during steam flushing) takes place due to establishing of thermodynamic balance according to the law of distribution of any substances between two immiscible solvents. Quantitatively this balance is characterized by distribution coefficient value K_d .

$$K_d = a_{st}/a_w = \text{const}, \quad (1)$$

where a_{st} и a_w — are activities of dissolved substance in steam and water phases.

For diluted solutions activities may be replaced with sufficient accuracy by corresponding concentrations:

$$K_d = C_s/C_w = \text{const} \quad (2)$$

This law is true for the same forms of compounds (molecules, ion pairs, ions) in both phases of solvent. Water and saturated steam being in balance with it, at every pressure (temperature) are two solvents having the same chemical nature with different densities and dielectric properties.

Transition of compounds into saturated steam due to dissolubility in it is preferential (selective) and strongly depends not only on system parameters but also on nature of compound.

For today, area of pressures $P_0 > 0,3 - 1$ MPa in which geothermal power plants work is not studied well. Only during recent years works in USA, Germany and England have lived up (EPRI 1993, EPRI 1999) with the purpose of determining K_d in the zone of steam pressures below 6 – 7 MPa (down to $P_0 > 3$ MPa). But all known studies of K_d values don't permit

determining distribution of impurities, salines, acids and other compounds in steam at GeoPPs that work within the low pressures zone $P_0 > 0,2 - 2,5$ MPa.

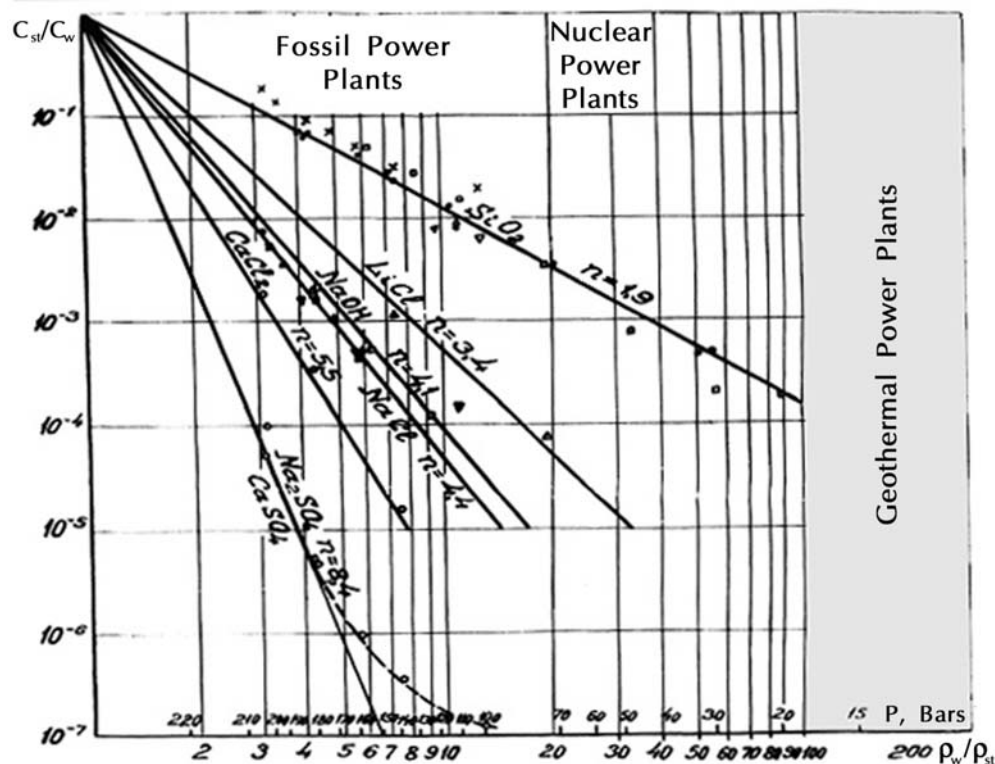


Figure 1. Dependence of distribution of impurities between saturated steam and water on proportion of phase densities constructed by M.A. Styrikovich in 1954.

At fig. 2 (EPRI 1993) recent test rig is shown having working chamber with volume of 900 cm³ which was used by Oak Ridge laboratory (USA) for studying distribution coefficients of *HCl*, *NaCl*, *NH₄Cl* etc.

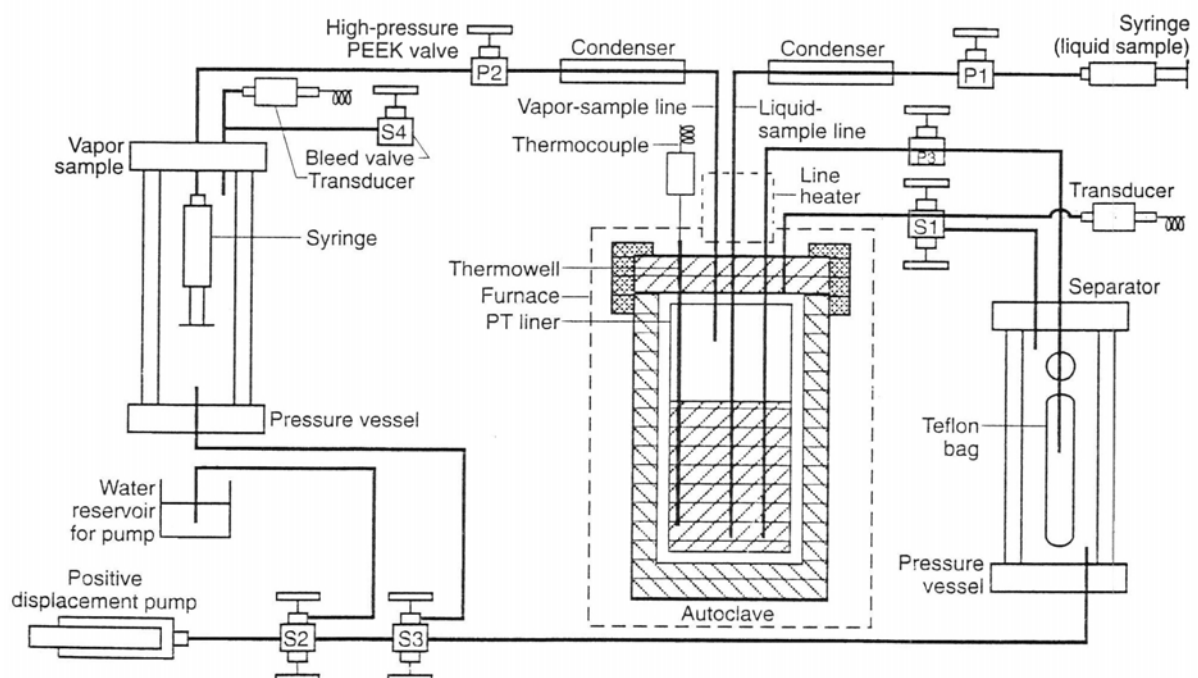


Figure 2. Test rig for determination of coefficients of impurities distribution between water and saturated steam at Oak Ridge laboratory (USA).

3. Dissolubility of impurities in saturated steam

Dissolubility of impurities in steam depends in many respects on form of existence (molecular or ionic) in which one or another compound is found in geothermal fluid.

Connection appearing between ions is very unstable, and ionic pairs have very limited time of existence. Total transition of all forms into steam thus will be as a rule almost entirely defined by transition into steam of substances being in water phase in molecular form. Only at very strong suppression of hydrolysis, i.e. at very high or, on the contrary, low pH values and correspondingly negligible share of molecules in geothermal fluid, participation of ions in steam pollution process may become noticeable.

$$\begin{array}{l} H_4SiO_2^{2-} + H_2O \leftrightarrow H_4SiO_3^- + OH \\ \quad\quad\quad \downarrow \\ H_4SiO_3^- + H_2O \leftrightarrow H_4SiO_4(water) + OH \end{array} \quad \begin{array}{c} H_4SiO_4(steam) \\ \updownarrow \end{array} \quad (3)$$
$$\beta = \frac{[H_4SiO_4]_w}{[H_4SiO_3^-]_w + [H_4SiO_4]_w} = \frac{[H_4SiO_4]_w}{[H_4SiO_4]_w^{tot.}} \quad (4)$$

$$K_h = \frac{K_w}{K_l} = \frac{[H_4SiO_4]_w [OH]}{[H_3SiO_4^-]} \quad (5)$$

It must be noted that apparent and true distribution coefficients exist. It is possible, measuring H_4SiO_4 in steam and knowing total silicon-contents of separate SiO_2 , to speak about apparent distribution coefficient, which is sometimes called carrying-out coefficient, presenting it as proportion:

$$K = K_d^{app.} = \frac{[H_4SiO_4]_{steam}}{[H_4SiO_4]_w^{tot.}} \quad (6)$$

True distribution coefficient is expressed by following proportion:

$$K_d^{true} = \frac{[H_4SiO_4]_{steam}}{[H_4SiO_4]_w} \quad (7)$$

True distribution coefficient of silicic acid between steam and water is a constant of phase balance characterizing true dissolubility of H_4SiO_4 in saturated steam and in water and being a function of densities of both environments.

It is obvious that at small ionic dissolubility apparent and true distribution coefficients are connected with each other by following proportion:

$$K_d^{app.} = K_d^{true} \beta \quad (8)$$

Implemented researches of geothermal turbines flowing parts condition showed that iron oxides are deposited in nozzle instrument first stages, consequently it is necessary to research ions and Fe compounds distribution coefficients for forecasting velocity of Fe deposition and reduction of open flow area of turbine nozzle grids. Analyses implemented at industrial stand proved that iron oxides (magnetite) transition well enough from water into saturated steam at high pressures and don't depend on pH value between 7.0 and 10.5 pH units.

Chlorides may pass from water into steam phase due to NH_4Cl , $NaCl$ and HCl dissolubility. Chlorides are brought to steam with the help of both HCl and NH_4Cl , distribution level depends on pH value and water phase temperature. Compound $NaCl$ is relatively insoluble in steam and has much lower dissolubility in steam than HCl and NH_4Cl (Styrikovich *et al.* 1959). At low ammonia concentration, HCl (especially for geothermal fluid having abyssal origin) is the main source of chlorides transition.

Geothermal fluid contains large amount of non-condensable gases (NCG) while their concentration in feeding water of traditional power plants is negligibly small. These gases decrease vacuum at turbine outlet and decrease its cost effectiveness so it is necessary to use the systems of non-condensable gases exhaust from condenser. Such systems use the working fluid (steam to ejectors) or electric power (water-circular pump or electric compressor), and in the long run this decreases total electric power generation by geothermal power plants.

NCG of geothermal fluid mostly consist of CO_2 , H_2S , CH_4 , NH_3 , H_2 and N_2 . Normally NCG concentration varies within the range from 1% to 2.5 % by mass. CO_2 and H_2S are most widespread gases for geothermal reservoirs. CO_2 plays important role in values changing of pH of reservoir water-carrying layers (Giggenbach 1980), and H_2S is the reason of hydrogen sulphide corrosion of geothermal power plants power equipment (Styrikovich *et al.* 1959).

During separation of steam-water mixture in steam preparation system redistribution of gases H_2 , N_2 and CH_4 from separate into saturated steam takes place, more dissoluble gases CO_2 , H_2S and NH_3 partially pass into saturated steam and partially remain in separate.

Values of distribution coefficients for NCG and some organic compounds are more than 1 ($K_d > 1$) and may be presented in upper part of radial diagram (fig. 3). As is well known, steam phase pressure consists of a sum of partial water steam and every gas individually, so it would be incorrect to depict dependence of non-condensable gases distribution on total pressure of steam environment. It's due to this that it is more correct to depict dependence of non-condensable gases distribution upon temperature (Belyanin *et al.* 1991). Distribution of these gases during separation of geothermal fluid depends on initial enthalpy, pressure and fluid temperature and also on its chemical characteristics.

Distribution coefficients of some impurities between steam and water phases also depend on pH value, presence of various chemical elements and their concentration in liquid phase.

Our researches (MPEI and “Nauka” SC) at Pilot Verkhne-Mutnovsky GeoPP permit today to fill this gap (Povarov *et al.* 2002) and to compose radial diagram practically for all the pressure range (proportion of phase densities) of steam used in power engineering. These experiments showed that in low pressure zone dependence $K_d = f(P)$ is not linear, at least for ions of Cl , Na and SiO_2 . For confirming this conclusion, of course, new additional data and studies will be necessary at various values of pH, temperature and pressure.

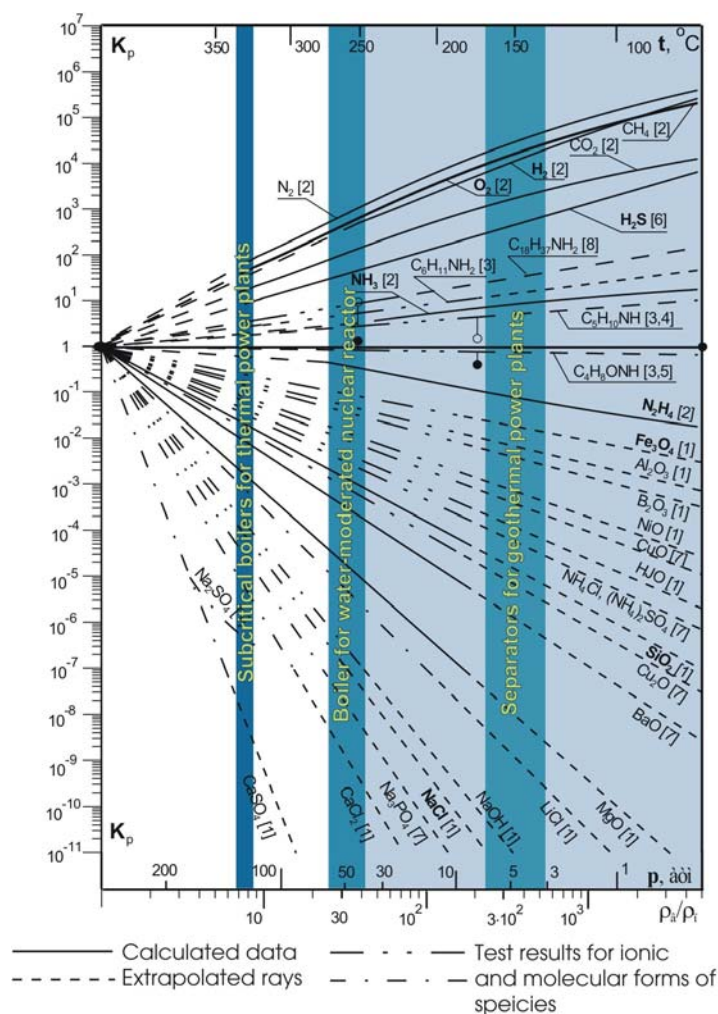


Figure 3. Diagram of distribution of impurities and gases between steam and water phases of fluid for thermal, nuclear and geothermal power plants.

4. Industrial test rig for studying distribution coefficients of impurities in geothermal fluid.

In high-capacity power plants coefficient of mechanical carry-over is equal to less than 0,01% by mass in wide pressure range (from 10 to 200 bars). And dissolubility in saturated water steam of various compounds of the same element may vary very strongly depending upon form of its being in water, increasing with pressure growth.

As was shown above, researches of K_d were implemented mostly in laboratory conditions in permanent regime at modeled working fluids using one or several chemical compounds.

In traditional heat power engineering steam generator feeding water after its corresponding treatment (liming and coagulation, deaeration, chemical desalination etc.) contains only parts per billion (ppb) of impurities and the steam coming to turbine is even purer.

In geothermal energy the steam coming to turbine is acquired as a result of separation of geothermal steam-water mixture coming from bowels of the earth along production well shaft. Geothermal fluid contains big number of nonvolatile and gaseous admixtures. As an example, in table below chemical composition of geothermal fluid liquid phase from production well No 049n of Verkhne-Mutnovsky area of Mutnovsky geothermal reservoir (Yuryev *et al.* 1998).

Table 3. Chemical composition of fluid liquid phase from well 049n at VM GeoPP

Well No	Chemical composition, ppm											
	pH	Cl	SO_4^{2-}	HCO_3^-	CO_3^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	SiO_2	As
049n	9,22	276	155,8	32,7	7,1	250	38	1,63	1,5	1,05	811	2,5

It can be seen that among impurities of fluid liquid phase corrosively active substances (chlorides, sodium, carbon dioxide etc.) and substances formed at definite deposition conditions (compounds of calcium, magnesium, silicon) are present.

Mass contents of all gases in steam-water mixture coming from above-mentioned well is equal to 0.42% by mass. Corrosively active compounds of H_2S , CO_2 etc. are present among gases.

In the process of operation above-listed impurities of water fluid are supplemented by products of corrosion of steam pipelines construction materials, of geothermal power plant FCDS equipment – nonvolatile iron oxides that may form deposits in turbine flowing part.

Above-stated demonstrates essential difference in quality of steam coming to turbine of traditional power plants as compared with GeoPP.

Researches on impurities distribution in geothermal fluid were implemented at industrial experimental plant of fluid collection and distribution system of Verkhne-Mutnovsky GeoPP. It must be noted that all researches were done at real equipment and at working parameters of GeoPP, thereby distribution coefficients indices were acquired considering steam flow humidity that must be used for forecasting and further calculations of impurities transition from geothermal fluid into steam coming to turbine.

Geothermal fluid collection and disposal system of Verkhne-Mutnovsky GeoPP (fig. 4) includes 4 separators, one flasher and one silencer. System consists of two separation stages consisting of

two separators each, common flasher constructively made by the same scheme as the separators, and common silencer.

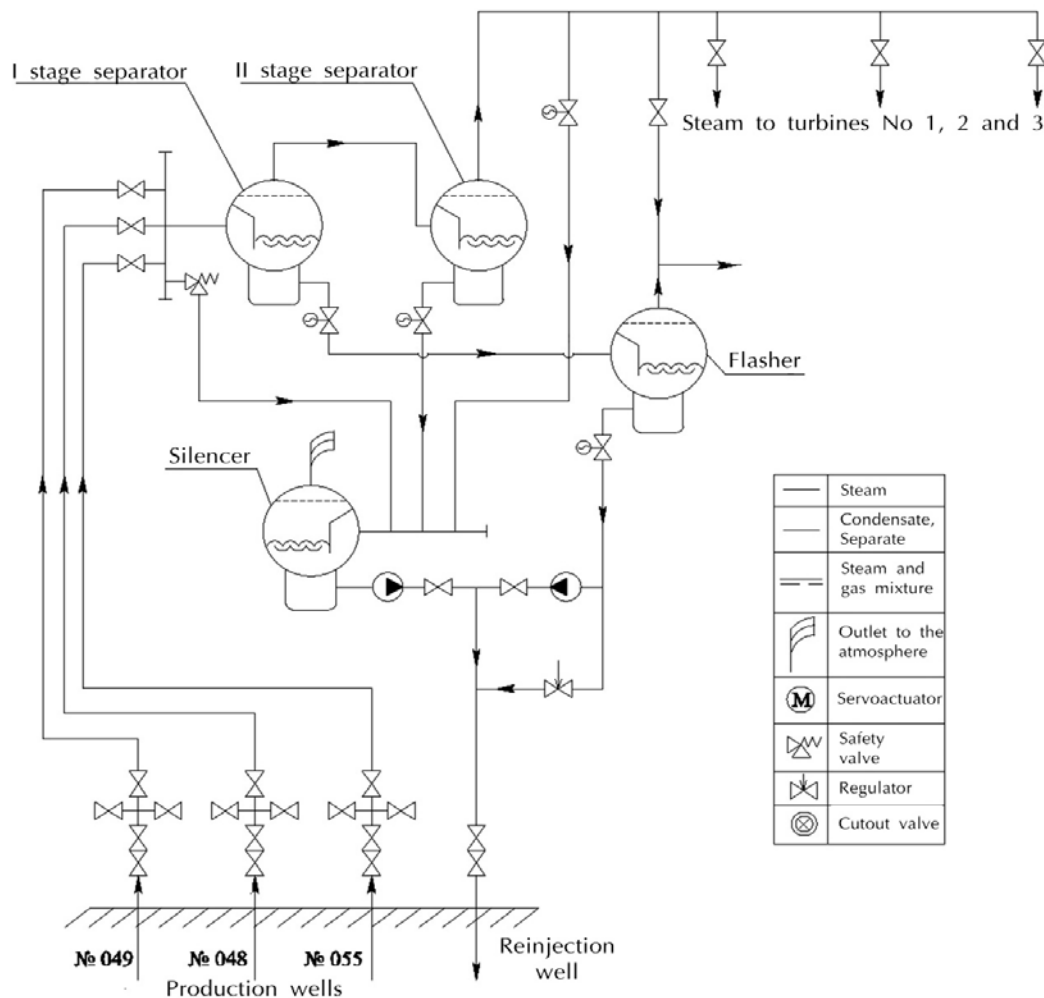


Figure 4 Simplified scheme of fluid collection and disposal system of Verkhne-Mutnovsky GeoPP.

Before separation first stage separation of one steam flow into two flows takes place through pairs of successive separators with steam capacity of 54 t/h each. Steam pipelines between separators of first and second stage separation have no heat insulation, and due to this condensation of part of steam and dilution of remaining drops that contain big amount of salines and other impurities by pure condensate with further removal of this moisture in second stage separators are achieved.

Separators design also permit to arrange if necessary in second stage separators the steam flushing by pure turbine condensate for better removal of impurities dissolved in steam and captured together with droplets carry-over.

Use of horizontal separators permits getting low steam velocities and gives high effectiveness of moisture removal practically for any geothermal fluid flow rate. Several principles of phase separation at once are used in them: centrifugal, jalousie and gravitational separation principles. Effectiveness of separators of such type is very high as calculated dryness extent of steam at separator outlet is higher than $x > 0,9995$, i.e. designers and manufacturers guarantee steam wetness $y < 0,05\%$ for various regimes of their operation (Povarov *et al.* 1997).

Measurement of steam humidity may be implemented with various methods among which mostly wide-spread are: calorimetric, radioactive and saline methods. Steam wetness after FCDS horizontal separators of VM GeoPP was determined by saline method, i.e. for determining steam wetness sodium ions concentrations in steam condensate and separated water were determined.

Accuracy of steam wetness determination depends not only on accepted methods of sodium ions concentration measuring but also on representativeness of collection of steam and water condensate samples, sample collectors design.

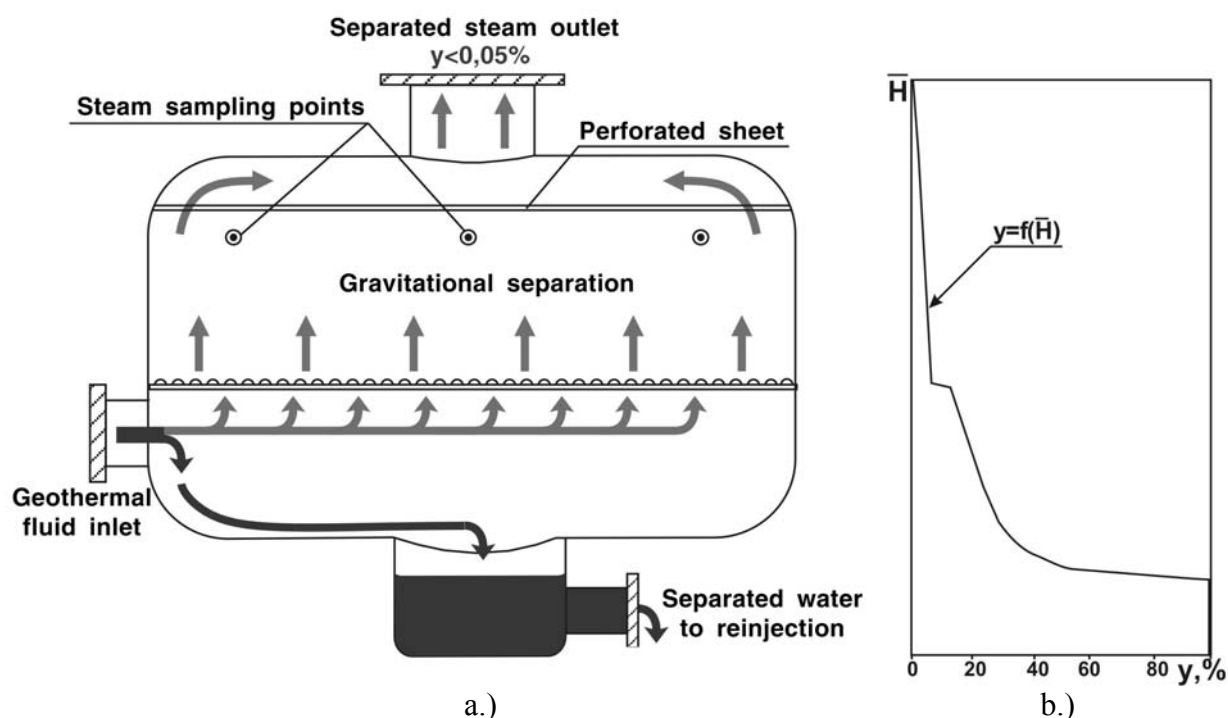


Figure 5 a.)-horizontal type gravitational separator;
b.)-dependence of steam humidity by instrument height

Collection of steam and separated water samples was implemented considering standardized requirements of branch-wise standards. Isokinetic conditions of sample collection were observed, sample collectors designs approved in boiler technique were used.

In table 4 results of measuring corresponding concentrations and calculated values of steam humidity after FCDS of Verkhne-Mutnovsky GeoPP are presented.

Table 4. Values of Na^+ concentration (ppb) in steam condensate and separate samples.

Sample collection point	Concentration of sodium ions in sample, mg/kg			Steam wetness $w = C_{\text{Na}}^{\text{st}} / C_{\text{Na}}^{\text{sep}} \cdot 100\%$
	$P_{\text{sep.}} = 8,5 \text{ bara}$	$P_{\text{sep.}} = 7,97 \text{ bara}$	$P_{\text{sep.}} = 6,23 \text{ bara}$	
Separated water from S-11	141,3	153,2	159,4	$0,0085 \div 0,017$
Condensate from S-21	0,024	0,013	0,023	

Measured wetness value is the evidence of high extent of effectiveness of horizontal type separators operation. Absolute value of salt-contents of Na^+ ions in steam upstream of turbine is less than 25 ppb which corresponds to steam quality norms after drum boilers with pressure of 70 bar and more. Chemical analysis of collected samples was implemented using modern chemical instruments – for example, chlorides concentration in steam and separate was permanently measured using flowing chloridometer XLP-1 with accuracy of 2 ppb, also photocolorimeter KFK-3 and ionic liquid chromatograph Dionex-2000i with measurement

accuracy of 2 ppb were used. Drop carry-over was negligibly small and permanently controlled using pNa-meter designed for micro-concentrations of sodium ions with accuracy of 2 ppb.

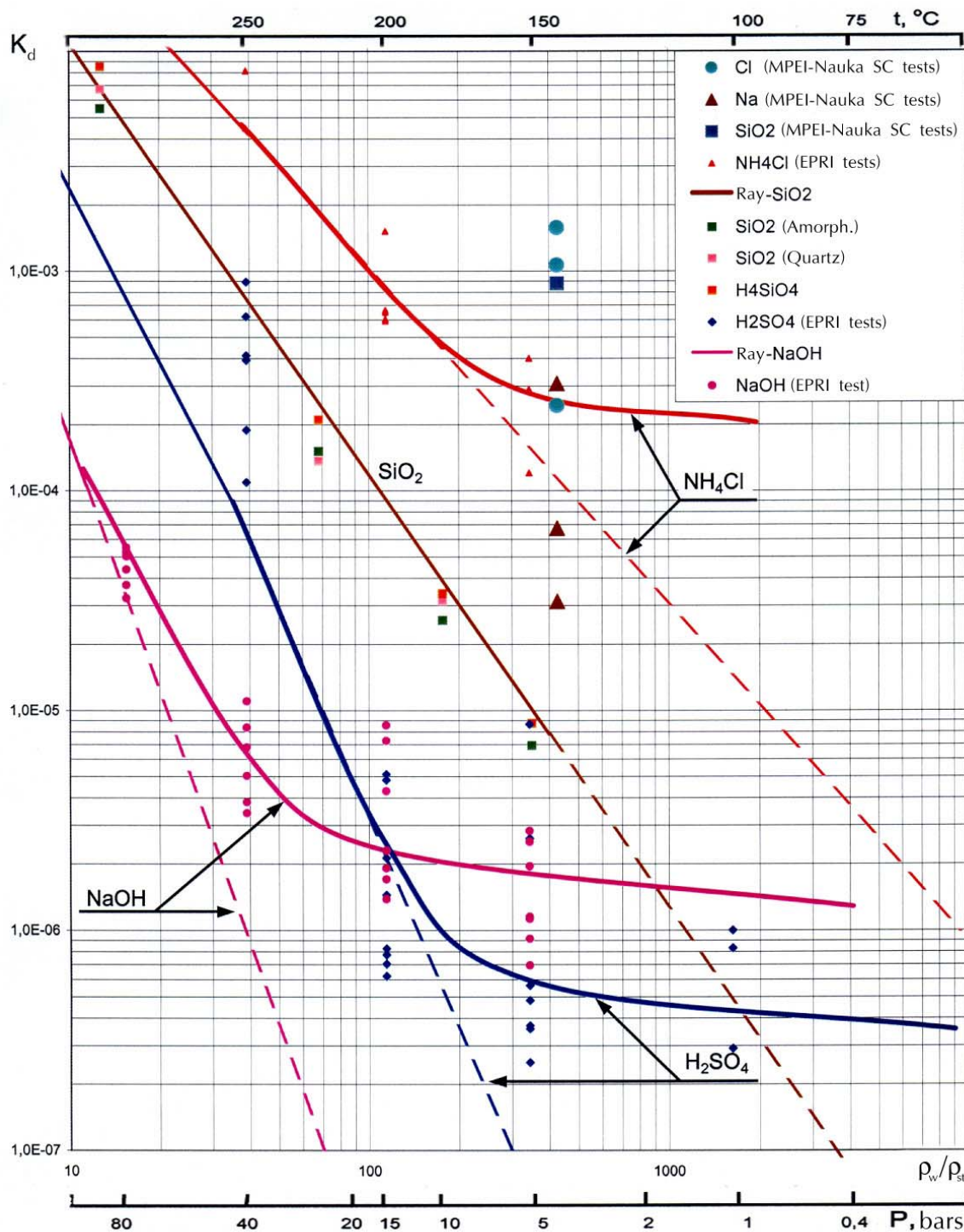


Figure 6. Experimental data on non-linear distribution of some impurities in low pressure zone.

These researches prove that process of distribution of impurities between steam and water in geothermal fluid is much more complicated than distribution of impurities in traditional power engineering.

Results acquired during these experiments presented at ray diagram (fig. 6) show that apparent distribution coefficients for Cl , Na^+ ions and SiO_2 are much higher than it was assumed basing on extrapolation of rays into low pressures area.

5. CONCLUSION

This work includes new experimental data on distribution of Cl , Na ions and SiO_2 between boiling water and saturated steam of geothermal fluid that were acquired during experiments at Verkhne-Mutnovsky GeoPP.

Necessity of these researches was discussed as well as main problems connected with geothermal power plants operation due to lack of information on distribution coefficients of impurities between water and saturated steam in steam preparation system.

It was determined that dependence of distribution coefficient on pressure $K_d=f(P)$ for some impurities in the low pressure zone may be not of linear character.

6. References

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