Proceedings World Geothermal Congress 2000
Kyushu - Tohoku, Japan, May 28 - June 10, 2000

PHYSICAL AND CHEMICAL PROCESSES OF GEOTHERMAL FLUID IMPACT ON METAL OF GEOTHERMAL POWER PLANT EQUIPMENT

O.A. Povarov, G.V. Tomarov, V.N. Semenov
Scientific and Training Centre of Geothermal Energy, Moscow Power Institute,
14, Krasnokazarmennaya st., E-250, Moscow, Russia

Keywords
Multi-phase flow, heat- mass transfer, corrosion, erosion, power plant, materials selection.

ABSTRACT

Features of multi-component geothermal fluid and physical-chemical processes of its impact on metal of geothermal power plant (GeoPP) equipment were considered. A model of corrosion mechanisms was studied and the results of GeoPP metal corrosion-erosion investigation are presented. Experimental data of corrosion-fatigue behavior of TA-5 titanic alloy and 15Cr11MF steel are discussed. Approaches to metal selection were studied, experimental polars and the Verchne-Mutnovsky GeoPP test rig are described.

1. INTRODUCTION

Active development of geothermal energy stimulated broadening of scientific investigations associated with hydraulic-gas dynamics, thermal physics, corrosion and other processes taking place on GeoPP equipment. However, studies, devoted to thermal mass transfer interaction with admixture behavior and corrosion processes in geothermal multi-component flows are almost absent**.**

Physical-chemical processes of corrosion, and aggressive components behaviour at heat mass-transfer surfaces significantly determine the type and intensity of corrosion-erosion influence of geothermal fluid on GeoPP equipment (Povarov, 1988; Tomarov, 1989; Heitmann, 1982; Povarov et al., 1995) Inter-phase transfers and substance redistribution complicate interaction of thermal mass transfer with corrosion effects and admixture behaviour in two-phase flow. In such conditions local concentrations of corrosion-aggressive gases and admixtures in liquid film directly contacting metal surfaces, can differ by several magnitudes from their concentration in the main flow. In this case hydrodynamic influence of the flow is performed through the steam-drop border layer and liquid film.

2. MULTI-COMPONENT GEOTHERMAL FLUID PROBLEMS

In most cases geothermal fluid of GeoPPs is a multi-component medium – wet steam flow with dissolved admixtures and non-condensable gases. Thus, in typical applications, its exergy (thermal drop to be utilised) does not exceed 700-800 kJ/kg (Britvin et al., 1999; Povarov, 1995; Povarov and Tomarov, 1995; Povarov and Tomarov, 1992), for thermodynamic wellhead parameters of: pressure, 0.2-2.0 MPa, and temperature, 120-250 °C (Povarov and Tomarov, 1995).

Geothermal fluid chemistry is characterised by presence of many chemical elements and compounds in various combinations. Fluid components having significant influence on corrosion and salt deposition include Na^{+}, Ca^{++}, Cl^{-}, and SiO2. The most important characteristics of geothermal fluids are the following: salinity (total dissolved solids) and pH. The following corrosion-aggressive gases generally prevail in gas the composition: carbon dioxide (60-95%) and hydrogen sulphide (2-15%) as well the hydrogen, methane, ammonia typically found in geothermal fluids.

Geothermal steam from a well many times exceeds live steam of conventional power plants in its contamination and wetness, and it is inferior in power potential. Therefore, a special Steam Preparation System (SPS) is required, providing necessary steam quality at the GeoPP turbine inlet. The main problems of GeoPP operation are associated with multi-component fluid influence on metal and equipment operation efficiency (Povarov and Tomarov, 1992). Reliability and efficiency of operation of the central and most expensive GeoPP component, the turbine, depend on the quality of geothermal steam.

Physical-chemical contamination of steam is not the same for different admixtures. (See Ray diagram Fig.1). (Styrikovich et al., 1969). The diagram was conditionally extended to the values of steam pressure at the thermal power plant turbine inlet (3-10 bar).

For comparison, the diagram shows zones of pressure of the steam at the turbine inlet of units with supercritical and subcritical parameters, i.e. nuclear and geothermal units. With decreasing pressure the quantity of admixtures declines from the steam to the liquid phase. This is particularly typical for the strong electrolytes ($CaSO_4$, $CaCl_2$, NaCl, NaOH…). The co-ordination number of strong electrolytes is rather high yielding n=4.0-9.0. For weak electrolytes n=1.0–3.0, and for solids (Fe_3O_4, Al_2O_3) n<1. This means that physical-chemical dissolution of admixtures in live steam of GeoPP turbines is considerably lower than that of conventional power plants. For example, NaCl dissolution in GeoPP live steam is almost two times lower than for nuclear power plants, three times lower than for units with supercritical parameters, and 10 times lower for units with subcritical parameters. As a result, the mechanism of admixture carrying-over with condensed moisture of GeoPP separator steam becomes a governing factor in the process of turbine live steam contamination. Admixture concentration in the liquid phase of geothermal fluid is considerably higher than in boiler water of conventional power plants that leads to substantial increases of admixtures in the liquid phase in the undissolved state. Therefore, even strong electrolytes with extremely low solubility in GeoPP steam ($Kp<10^{-10}$) can partition to turbine live steam in substantially high concentrations in the undissolved state.

Geothermal fluid movement through the GeoPP circuit is accompanied by considerable changes in its phase state, thermodynamic parameters (temperature, pressure, enthalpy), mode characteristics (flow velocity, turbulence) and chemistry.

Different combinations of hydrodynamic (mass transfer) and corrosion factors of geothermal fluid impact leads to different types of metal destruction. The phase state of the fluid is of great influence. It determines the nature of corrosion effect (chemical in dry steam, electrochemical – in wet steam and water) and its intensity.
The following types of metal destruction may take place in up-to-date geothermal power plants (Povarov, et al., 1992; Povarov et al., 1991):

1. general corrosion (GC);
2. pitting corrosion (PC);
3. contact corrosion (CC);
4. erosion-corrosion wear (ECW);
5. corrosion cracking under load (CCL);
6. drop impact erosion (DIE);
7. cavitation erosion (KE);
8. abrasive erosion (AE).

Identification based on criterion modelling of mechanisms of metal destruction is the most important stage in investigation of physical-chemical processes and the causes of particular GeoPP equipment failure.

This approach allows formulation of an identification chart indicating the places of expected occurrence of different mechanisms of metal destruction (ref. to Fig. 2). In this case it is important to use smoothed data of medium flow rather than local (i.e. in border layer and wall zones) characteristics and parameters of mass transfer, admixture concentration and corrosion factors.

2. EROSION-CORROSION WEAR OF METALS

Experience (Povarov et al., 1991) shows that one of the most wide spread types of destruction of GeoPP working path metal is erosion-corrosion wear (ECW). GeoPP units in contact with wet-steam or water flows are subjected to erosion-corrosion. “Erosion-corrosion” in the geothermal fluid is an interdependent process, including—formation of a protection layer of corrosion products on the metal surface and its hydrodynamic (mechanical) destruction and dissolution under flow influence.

Mass-transfer processes in the steam-channel border layer and in the wall-liquid film determine erosion factor intensity. The mechanism of metal transition to the flow (or metal losses as a result of ECW) in geothermal fluid exhibits a series of sequential stages which are symbolically shown on Fig. 3.

Movement of geothermal fluid increases delivery of corrosion active agents to the metal and the gradient of the concentration of dissolved corrosion products near the sulfide layer. In this case mass transfer is accomplished with molecular diffusion and mutual movement of the corrosion product and liquid:

$$J_m = C \cdot \rho \cdot u - \rho \cdot D \cdot \mathrm{grad}C \qquad (1)$$

For parallel-sided long channels $\frac{\partial c}{\partial x} << \frac{\partial c}{\partial y}$

This allows the equation of convective diffusion in non-dimensional form to be expressed as:

$$\frac{\partial Sh}{\partial y} + Sh \cdot Re \cdot Sc \cdot u_y = 0 \qquad (2)$$

where:

Sh—Sherwood number
Re—Reinolds number
Sc—Shmidt number

Erosion-corrosion in wet-steam has a number of principal differences compared with the process of erosion-corrosion in water. Movement of two-phase flow is accompanied by formation of liquid film on the streamlined surface (Povarov, 1988; Tomarov, 1989). In such conditions, the flow behaviour of liquid film and mass-transfer characteristics in the two-phase border layer determine the erosion factor (discussed in more detail in (Tomarov, 1989). As shown above, the erosion factor of erosion-corrosion is characterised by the following determining parameters: Re, Sh, Sc. For two-phase fluid the values of these parameters are to be considered separately in water (liquid film) and steam. The values of these same parameters in steam and liquid film differ by several times (ref. Table No1). High values of Shmidt number for liquid film indicate that convective mass transfer in liquid film even at low flow velocities prevail upon molecular diffusion. Therefore, in the two-phase liquid border layer the manner of cross mass transfer in the steam and in film sub-layer is not the same. In the steam-drop layer, turbulent diffusion of small particles prevails. In film layer—convective transfer the process is intensified by wave movement of the film.

Characteristics of steam flow and liquid film movement (laminar, turbulent) determine the form and intensity of mass transfer processes, as an erosion factor. Therefore it is advisable to accept the Re, Sh, Sc numbers for water medium; for wet steam flow -- Re_s, Re_{film}, Sh, Sc are the main erosion-corrosion parameters reflecting hydro-gas-dynamic influence. Tests have determined dependence of erosion-corrosion wear as a function of flow regimes of the steam flow (Re_s) and liquid film flow (Re_{film})

(ref. to Fig. 4) (Tomarov, 1989; Povarov et al., 1986).

The erosion-corrosion process in two-phase flow is accompanied by redistribution of impurities between the steam and liquid phases.

3. CORROSION CRACKING OF METAL ON WORKING BLADES

Up to 40% of failures and emergency shutdowns of GeoPP are connected with the failures of turbine components and working blades (Povarov *et al.,* 1991). The main cause of these failures is metal corrosion cracking (MCC) under cyclic tensions. Cracking is promoted by chloride in non-uniformity of salt deposition and pittings (Povarov et al., 1986; Allegrini and Benvenuti, 1970).

A method to control this MCC phenomenon may be the use of titanium alloys and high-chromium steels. Wide application of titanium alloys for manufacture of high-duty GeoPP components is restrained due to the absence of data of their corrosion-fatigue behaviour in geothermal fluid.

To determine the potential of GeoPP working blades manufacture using titanium alloys and high-chromium steels, special investigations were conducted. The study of corrosion-fatigue behaviour of titanium alloy TA-5 and martensite-ferrite steel 15Cr11MF was conducted in an air environment, simulated geothermal fluid, and in geothermal fluid containing hydrogen sulfide. The geothermal fluid chemistry was the same as the environment at Mutnovsky geothermal site.

Endurance tests were carried out on machines, making pure bending of rotating specimen with the test base of $5 \cdot 10^7$ cycles. The results of corrosion-fatigue tests of smooth specimens from titanium steel TA-5 are presented on Fig.5a. The fatigue limit of TA-5 in air is at the level of 280 MPa. The ratio of fatigue limit to ultimate strength under alloy tension is only 0.32 σ_w (σ_w=872 MPa). Tests of alloy TA-5 in the geothermal fluid showed a decrease of fatigue limit by 11% (σ_w^{corr}=250 MPa). Mutual effect of geothermal fluid and hydrogen sulfide leads to an additional decrease of fatigue limit of TA-5 by 12% (σ_{-1}^{corr}=220 MPa) compared to tests in geothermal fluid, and by 22% compared to tests in the air.

Fig.5b presents the results of fatigue tests of 15Cr11MF specimens. The conditional fatigue limit in geothermal fluid was determined at the level of 90 MPa, i.e. the fatigue limit decreased by 77% compared to tests in the air. In the presence of hydrogen sulfide in geothermal fluid the fatigue limit for steel 12Cr11MF has not been realised even after 80% strength reduction. Steel 12Cr11MF proved to be more sensitive to placing of tension concentration than TA-5.

Thus, the tests showed high corrosion-fatigue tolerance of the Russian titanium alloy TA-5 in the geothermal fluid, that provides ground to consider its potential use for manufacture of working blades GeoPP turbines.

4. SELECTION OF METAL FOR GEOTHERMAL POWER UNIT EQUIPMENT

One of the most radical ways to increase reliability and durability of power equipment in geothermal power plants is the optimal choice of erosion-corrosion resistant metals. Currently, making decisions on the choice of metal for GeoPP is based on operational experience and test results (Povarov *et al*., 1986; Gallup and Farison, 1998). Selection of metals for GeoPP equipment has to meet operational, technological and economical requirements. Technological and economical requirements are of great importance under serial manufacture or under manufacture of metal-intensive equipment. In most cases operational requirements are playing a determining role.

Nowadays, evaluation of the fitness of metal strength properties for given operational conditions, as a rule, is not a complicated task and is performed using well-developed techniques of calculation. Estimation of their corrosion and erosion resistivity under operational conditions is a more complicated, but less important task in the metal selection process.

The existing approaches and methods of metal selection do not allow for phase state of fluid flow hydrodynamics, and are often limited to consideration of single-phase (water) flow influence on metal. It is necessary to carry out metal selection for geothermal equipment based on a systematic, comprehensive approach, taking into account the role and influence of different parameters and characteristics of medium quality, metal and flow hydro-gas-dynamics. The conceptual expert system developed allows clear identification of destruction type and is based on a criteria approach.

Based on the knowledge of physical-chemical processes of metal destruction, and also on GeoPP operational experience and test data, the system of GeoPP metal destruction mechanisms was developed. Identification of influence type (or destruction mechanism) of medium on metal is an important stage for consideration of erosion and corrosion resistivity of GeoPP components metal. (Ref. to Fig.6). The characteristics of geothermal fluid have considerable influence on the reflection and realisation of different mechanisms of destruction. For the expert system of metal selection, fluid specification is the first stage. The following types of geothermal fluids are the most typical for the working circuits of GeoPP:

1. Steam;
2. Wet steam (<50%);
3. Steam-water (>50%);
4. Brine;
5. Condensate;
6. Steam-gas;
7. Water;
8. Special conditions (extreme);
9. Organic working fluids

The phase state, dissolved solids, gas content, oxygen content, and temperature characterize the type of geothermal fluid processed. In every geothermal fluid specification only certain types of metal destruction may appear. This means that specification of geothermal fluid focuses the list of the possible metal destruction types. The type or mechanism of the metal destruction in the given medium depends on a combination of corrosion and erosion factors. The type and the intensity of the corrosion factor can be determined by several criteria in the form of corrosion rate. In turn, depending on the above, the possible choice of metal for construction and the possible destruction types are determined for the given particular local conditions.

At the next stage, hydrodynamic (mechanical) activity of the medium for the particular case is determined. Reflection of the erosion type of geothermal medium flow influence on the metal depends on this parameter. On the basis of the comparison of the fluid corrosivity and mechanical activity the type of the destruction for each particular case can be determined. This also can be a combination of two or more types of destruction.

The next step, is determination of metal groups of alloys suitable for the given conditions using the data bank of the metals compiled by the "type of destruction" and the data bank of the metals compiled by "groups of equipment". After a group of metals principally suitable for given conditions is selected, the next stage will be estimation of the metal destruction intensity. The use of the data bank of the "resistance of the previously tested metals" and procedures on determination of the intensity of metals destruction (based on the known regularities and features of these processes) yields an increase of accuracy and reliability of the result. The comparison of the resistance of the metals gives the possibility to compile the metal's priority list.

The developed expert system of the metals selection allows for optimization of metal choice based on economic aspects and includes all existing international practice special- warnings on the use of the chosen metals. Using the data bank of the potential constructive metals its possible to obtain a list of optimal metals in the form of the Russian metal marks or foreign analogs (ref. to Fig. No 6).

The metal selection expert system consisting of PC-software permits accelerated and correct decisions for metals choice of equipment for geothermal energy systems.

REFERENCES

Britvin, O.A., Povarov, O.A., Klochkov, E.F. (1999). Verchne-Mutnovskaya geothermal power plant. *Jnl. Teploenergetika*, No 2

Gallup, D.L., Farison, J.R. (1998). Testing of materials in corrosive wells at the Geysers geothermal field. *Proc. 20th NZ Geothermal Workshop*

Heitman, H.G., Kastes. W. (1982). Erosion-Corrosion in Wasser-DamfKreslaufen-Ursachen und Gegenmassnamen. *VGB. Kraftwerkstechnik*, V. 62, No 3, pp 211-219

Lichti K.A. (1995). Selection and use of materials for geothermal energy applications using computer based technology. *Proc. of the World Geothermal Congress, Italy*, pp 2981-2986

Povarov, O.A. Tomarov, G.V. (1992). Problems of multi-phase geothermal fluids. *Jnl. Teploenergetika*, No5, pp. 66-71

Povarov, O.A., Semenov, B.N. (1986). Aggressive medium influence on steam turbine reliability. *Jnl. Teploenergetika*, No 10, pp. 33-38

Povarov, O.A., Stanisa, B.V., Tomarov, G.V. (1986). Erosion-korrosions-abragung von metall in Stromungsteil Einer NaB dampfturbine. Jnl. *Brenstoff-Warme-Kraft*, Vol. 38, No. 12, pp.534-538

Povarov, O.A., Tomarov, G.V. (1995). Geothermal power plants for electricity generation and heating purposes in Russia. *Proc. of the World Geothermal Congress. Italy*, Vol. 3, pp. 2115-2118

Povarov, O.A., Tomarov, G.V., Kutyrev, S. Yu., Velichko, Ye.V. (1991*). Problems of salt depositions and wear of geothermal power unit components*. ZNIITEIItyazhmash, Moscow

Povarov, O.A., Tomarov, G.V., Zharov, V.N., Kutyrev, C.Yu. (1992). Causes of damages and ways to increase reliability of GeoPP equipment. *Jnl. Energeticheskoye Stroitelstvo*, No 2, pp. 14-20

Povarov, P.A., Tomarov, G.V., Semenov V.N. (1995). Russian geothermal resources and problems of metal erosion-corrosion of geothermal power plants. *Proc. of the World Geothermal Congress. Italy*., Vol. 4, pp. 2433-2441

Styrikovich, A.A., Martynova, O.A., Miropolsky, Z.L. (1969). *Processes of steam generation on power plants*. Energia, Moscow

Tomarov, G.V. (1998). Erosion-corrosion of structure materials in saturated-steam turbines, *Jnl. Teploenergetica*, No 7

Table 1. Some physical characteristics and similarity criteria of liquid film flow in steam

Medium	D, m^2/c	ν, m^2/c	u, m/c	h, m	Se	Re	Pe=Re-Sc
Steam	10^{-5}	$2*10^{-5}$	20÷10	10^{-3}	1÷10	10^4÷10^6	10^4÷10^7
Liquid film	10^{-9}÷10^{-10}	$3*10^{-7}$	0.1÷0.5	10^{-5}	500	10÷200	10^3÷10^4

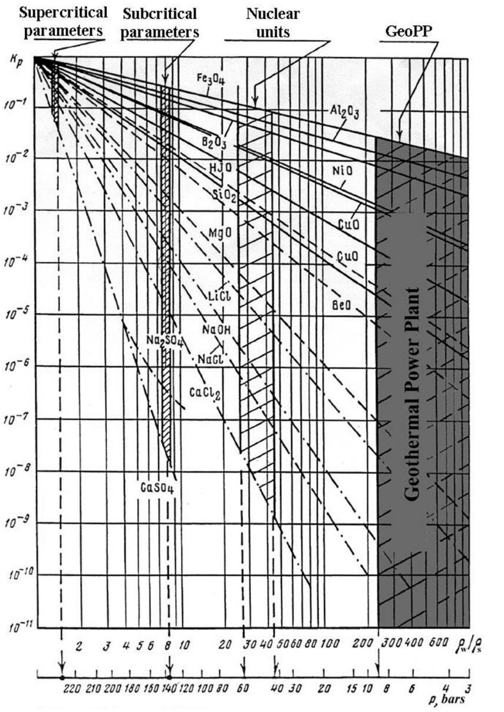


Fig. 1 Ray diagram of admixture distribution ratio between steam and water:

━━ – test data; ‒ ‒ – calculated data;

I; II; III; IV – steam pressure at the turbine inlet of units with supercritical parameters, subcritical parameters, nuclear power plant units and GeoPP units accordingly

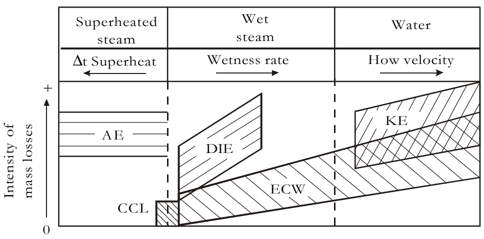


Fig. 2 Identification chart of forecasted realization of mechanism of geothermal heat-fluid influence on metal of Verchne-Mutnovsky GeoPP:

AE – abrasive wear; DIE – drop impact erosion; KE – cavitational erosion; CCL – corrosion cracking under load; ECW – erosion-corrosion wear

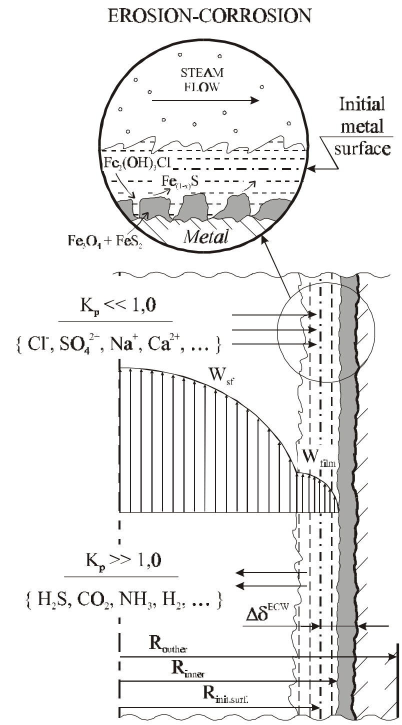


Fig. 3 Mechanism of metal erosion-corrosion under geothermal fluid

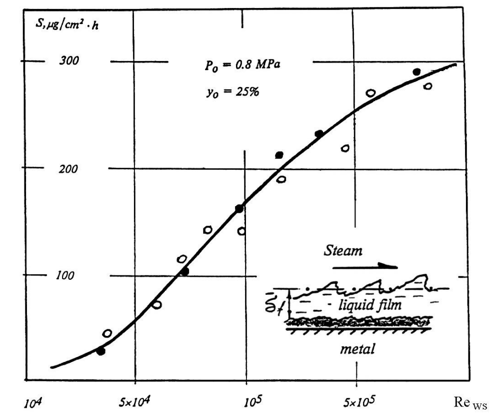
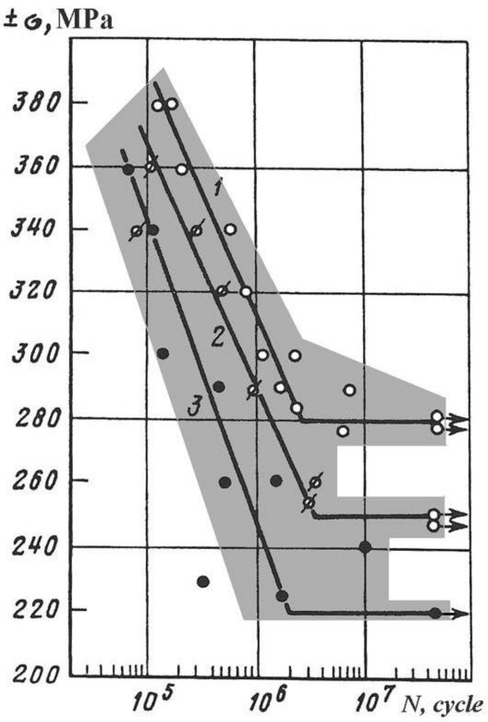
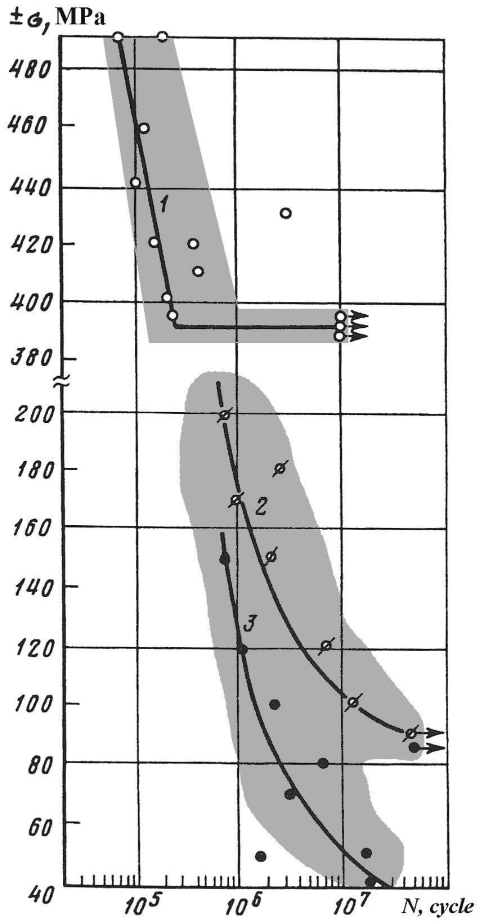


Fig. 4 Erosion-corrosion velocity of steel under wet steam (Re_{ws})



a)



b)

Fig. 5 Fatigue characteristics of smooth specimens of titanium alloy TC-5 (a) and steel 15Cr11MF (b) in air – 1; geothermal fluid – 2 and in geothermal fluid with hydrogen sulphide –3.

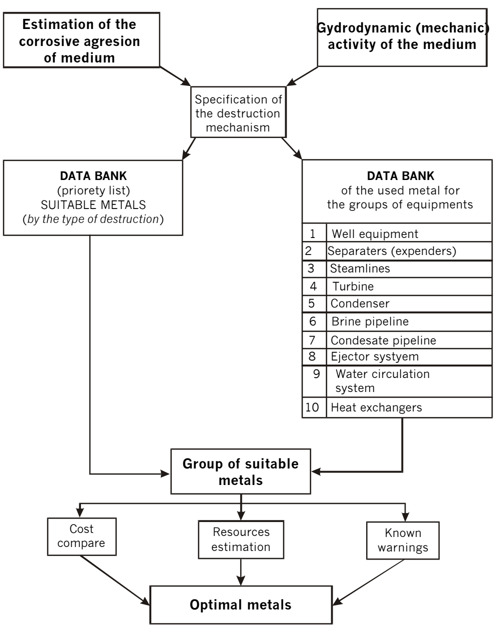


Fig. 6 Algorithm of metal selection scheme for GeoPP equipment