GAS BUBBLE-FACILITATED TRANSPORT OF METALS IN LITHOSPHERE①

Wen Baihong
Scientific Research Institute of Petroleum Exploration and Development of CNPC, 20, Xueyuan Road, Beijing 100083, P. R. China
O.F. Putikov
St. Petersburg State Mining Institute, 2, 21st Linija, St. Petersburg 199026, Russia

ABSTRACT A physicochemical model for transport of mobile forms of occurrence of elements by gas bubbles in porous medium—gas bubble-facilitated transport of metals in the lithosphere is proposed and its corresponding mathematical model is discussed. The physico-chemical model consists of three phases: water with dissolved metallic elements, gas bubbles and solid matrix of the porous medium. In the model the gas bubbles act as carriers to transport the elements in the pore water from the depth in the lithosphere to the Earth's surface. In the process of transportation the elements dissipate in porous rocks and consequently a new kind of geochemical halo—jet halo of dispersion is formed in the rocks. In order to describe the transport and fate of the elements in the porous rocks a nonlinear quasiconvection mathematical model is developed, in which the transport of elements is modeled by a quasiconvection of gas bubbles with the elements and the interaction of elements with the porous medium is represented by a second-order chemical kinetics. A finite difference scheme is provided to solve the nonlinear quasiconvection model. From the numerical solutions a stabilization effect of concentration front in the transportation of elements in the porous medium is discovered. The sensitivities of the stabilization effect to model parameters are analyzed. To verify the reality of the mathematical model, physicochemical modeling experiments are conducted. The obtained experimental data support the proposed model in this work.

Key words gas bubble-facilitated transport of metals mobile forms of occurrence of elements stabilization effect jet halo of dispersion porous medium

1 INTRODUCTION

Studies on distant migration of elements from the depth of the earth have increased since 1980. One of these studies is focused on the transport of trace elements in the gases, released from the depths of the lithosphere. Emanation of gases in depths is a well-known phenomenon in connection with active volcanism and with deposits of hydrocarbons. Recent studies have shown that a relatively stable gas flow is observed at a depth of 700 m or deeper[1-3], and that the gases ascend in the form of gas bubbles and transport certain trace elements (Co, Ni, Mo, Cu, Pb, Zn etc.) upwards in themselves[4-7]. It is believed that in the process of distant transportation of mobile forms of trace elements by gases from the depth to the earth's surface, the elements will dissipate in the rocks because of interaction between them and, consequently, form a new kind of geochemical halo—jet halo of dispersion[8-12]. The essential features of the new kind of geochemical halo are: (1) jet shape, stretching from the source to the Earth's surface, and (2) vertically directed transportation of elements in the lithosphere.

Based on studying the new kind of geochemical halo, a series of geoelectrochemical

① Project of the Program of Advanced Institutions 3/H190-353 supported by Ministery of Education of Russia
Received Nov. 13, 1997; accepted Sep. 24, 1998

methods (partial extraction of metals CHIM, diffusive extraction of metals MDE, prospecting by forms of the occurrence of elements MPF, thermomagnetic geochemical method TMGM and others) have been developed. In the past two decades by using geoelectrochemical methods, tens of ore deposits have been found in the former USSR. But details of the mechanism of transportation of elements from the source to the earth's surface, however, is poorly understood. The object of the present work is to provide a physicochemical model of transportation of elements and its corresponding mathematical relationship between the model parameters and the formation of the jet halo of dispersion.

2 PHYSICOCHEMICAL MODEL

Different from traditional lithochemical halos, the characteristics of jet halo —weak dependence of its amplitude and width on the depth of the source, correspondence of its width to the projection of the source on the earth's surface and correlation of its content with that of the source[13], are determined by the mechanism of formation of the jet halos in the rocks. One of the possible mechanisms is the gas bubble-facilitated transport of metals[5,12]. The obtained experimental results[14,15] have verified that the colloidal and suspended gas bubbles can capture the mobile forms of metals (ions or radicals of metals) and transport them in a nearly vertical direction towards the surface of the porous medium. There are two ways for gas bubbles to transport the elements: (1) in the gaseous form of volatile compounds of metals in the gas bubbles and (2) in the sorbed membrane on the surface of the gas bubbles —natural ion flotation (Fig.1). In the process of penetration through the porous medium the sorbed/included ions or radicals of metals interact with gas bubbles, water and rocks. As a result, the elements of metals dissipate in the rocks and a jet halo is formed in the overlaying rocks.

This physicochemical model applies under the following conditions:

(1) There are three phases in the porous medium: water with dissolved metallic elements (ions or radicals of metals), colloidal gas bubbles and solid particles of the porous medium (Fig. 1);

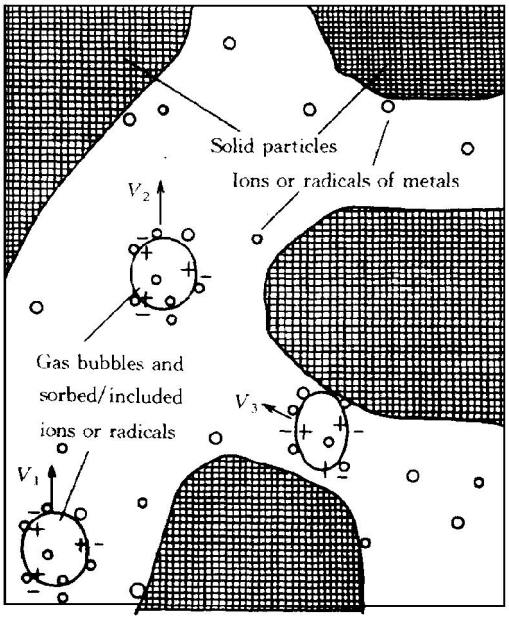

Fig.1 Model of gas bubble-facilitated transport of elements in porous medium
V_1, V_2, V_3 —Effective speed of gas bubbles

(2) The flows of gas bubbles penetrate upwards from below the source of metals through the porous medium, of which radius is less than that of the pore (Fig.2, zone 1);

(3) The gas bubbles capture volatile compounds of the metals in their inner and ions or radicals of the metals on their surface by interfacial forces (Fig.2, zone 2);

(4) The gas flows transport some of these metals upwards and in the meantime form jet halos in the rocks (Fig.2, zone 3).

3 MATHEMATICAL MODELING

The corresponding mathematical model can be written as a nonlinear quasiconvective equation with the second-order chemical kinetics[16]:

$$D\frac{\partial^2 C}{\partial z^2} - V_{\text{eff}}\frac{\partial C}{\partial z} - \frac{\partial q}{\partial t} - \frac{\partial C}{\partial t} = 0 \qquad (1)$$

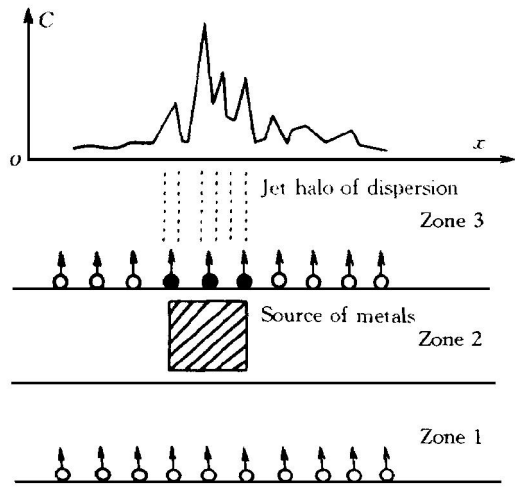

Fig.2 Scheme of the physicochemical model of formation of jet halo in lithosphere
● —Gas bubbles with sorbed/included ions or radicals of metals; ○ — Without them

$$\frac{\partial q}{\partial t} = \beta C(q_{max} - q) \quad (2)$$

where C—volume concentration of the mobile forms of metallic elements in pore water; D—hydrodynamic dispersion coefficient; V_{eff}—effective speed of quasiconvection of the dissolved elements (ions or radicals), related with the penetration of gas bubbles; q—concentration of sorbed elements on the solid matrix of porous medium; q_{max}—maximal concentration of sorbed elements; β—adsorption rate coefficient of elements; t—time; z—distance from the source in vertical direction, origin of z is on the surface of the source.

Under the initial condition

$$q|_{t=0} = 0$$

we have

$$q = q_{max}[1 - \exp(-\beta\int_0^t C\mathrm{d}\eta)] \quad (3)$$

Taking derivation of Eqn.(3) with respect to t and inserting in Eqn.(1), we have

$$D\frac{\partial^2 C}{\partial z^2} - V_{eff}\frac{\partial C}{\partial z} - \beta q_{max} C \times \exp(-\beta\int_0^t C(z,\eta)\mathrm{d}\eta) - \frac{\partial C}{\partial t} = 0 \quad (4)$$

It is a nonlinear integrodifferential equation.

Under the initial and boundary conditions

$$C|_{t=0} = 0$$
$$C|_{z=0} = C_0 \quad (5a)$$
$$C|_{z\to\infty}$$

for infinite boundaries or

$$(V_{eff}C - D\frac{\partial C}{\partial z})|_{z=H} = \chi C|_{z=H} \quad (5b)$$

for finite depth,

where C_0—concentration of elements in the source; χ—coefficient of transition of elements on the earth's surface to the atmosphere; H—the depth of the source from the earth's surface. Eqn.(4) can be solved numerically by a partially implicit scheme of finite difference method and iteration method as follows[17]:

$$-(0.25c + 0.5s)C_{j-1}^{n+1} + [1.0 + s + \beta q_{max}\Delta t\exp(-\beta\sum_{k=1}^{n+1} C_j^k\Delta t)]C_j^{n+1} + (0.25c - 0.5s)C_{j+1}^{n+1} = (0.25c + 0.5s)C_{j-1}^n + (1.0 - s)C_j^n + (-0.25c + 0.5s)C_{j+1}^n \quad (6)$$

where $c = \frac{V_{eff}\Delta t}{\Delta z}$, $s = \frac{D\Delta t}{\Delta z^2}$, $\Delta z\Delta t$—finite elements by z and t; C_j^n—approximated concentration of elements in the discrete distance j and time n. In simplified cases the analytical solutions can be obtained for the problem Eqn.(4). Comparison of the analytical with the numerical solutions confirms the accuracy and precision (squared root relative error is 10^{-4}) of the numerical solution. From numerical solutions (Fig.3) it is obvious that the process of quasiconvection stabilizes after a certain transition time T_s, when the concentration front advances at a stabilized speed V_s and the form of the concentration front changes insignificantly.

Sensitivity analysis of the stabilization effect to model parameters V_{eff}/D, q_{max}/C_0 and β in the transient process of transportation of elements (Fig.4) shows that in the early stage of the transient process because of diffusion the speed of the advance of the concentration front V is greater than the stabilized speed V_s, but in the later stage because of adsorption the speed of advance V is decreased sharply. After transition time T_s the transient process stabilizes at the sta-

bilized speed V_s, having the following empirical formula:

$$T_s = \frac{11}{\beta} \times \left(\frac{1}{q_{max}} + \frac{1}{C_0}\right) \quad (7)$$

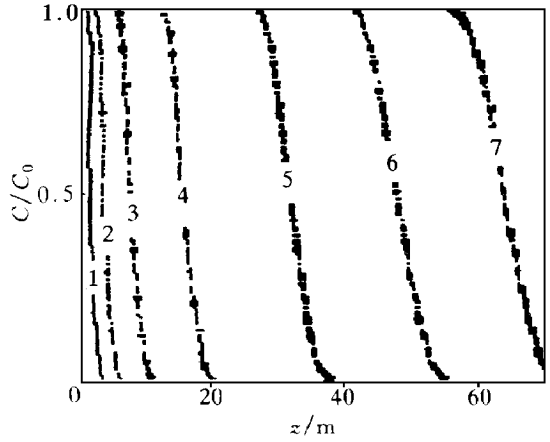

Fig.3 Numerical solution of concentration distribution of elements by Eqns.(5) and (6): $V_{eff}/D = 10\ m^{-1}$, $q_{max}/C_0 = 0.1$, $\beta = 10^{-7}\ m^3/s$
1 — t = 231; 2 — t = 463; 3 — t = 926; 4 — t = 1 852; 5 — t = 3 704; 6 — t = 5 556; 7 — t = 7 407 days

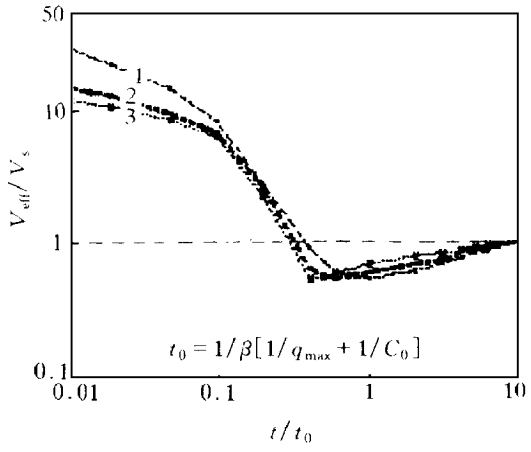

Fig.4 Sensitivity analysis of stabilization effect on model parameters: $q_{max}/C_0 = 10$, $\beta = 10^{-7}\ m^3/s$
1 — $V_{eff}/D = 1$; 2 — $V_{eff}/D = 10$; 3 — $V_{eff}/D = 100\ m^{-1}$

$$V_s = \frac{C_0 V_{eff}}{C_0 + q_{max}} \quad (8)$$

In this way after sufficient time the concentration front will reach the earth's surface with a certain concentration of metals C_s. This agrees with the field observations[13] in that concentration of metals insignificantly varies with depth, but mainly depends on content of metals in the sources at depth.

4 PHYSICOCHEMICAL MODELING

In order to examine the reality of the physicochemical model and its corresponding mathematical model, a number of laboratory experiments have been carried out[12, 14, 15]. In the first series of experiments a capillary model without consideration of interactions of gas bubbles and dissolved elements with the wall of the capillary is simulated by a vertical glass tube of height 790 mm, which is filled with water to height 750 mm and a solution of $KMnO_4$ (concentration of Mn is 700 mg/L) or $CuSO_4$ (concentration of Cu is 800 mg/L) in the lower part of the tube to height 150 mm. A flow of air bubbles of radius 0.01 ~ 0.1 mm is fed into the tube from the bottom with the help of a bubble generator. There are four openings on the side of the tube for taking samples, which are analyzed by instrument of modified atomic absorption spectroscopy AAS (with a sensitivity of 0.001 g/L). In these experiments Cu is in the form of simple cation Cu^{2+} and Mn is in the form of complex anion, MnO_4^-.

In the first experiment with tape water in the tube after 5 h of passing gas bubbles through the capillary model the concentration of Cu in the upper part of the tube, 0.021 g/L, is about the same as the background concentration 0.001 ~ 0.032 g/L (Fig.5(a), curve 1); but the concentration of Mn is increased from background concentration 0.025 ~ 0.060 g/L to 0.11 g/L (Fig.5(b), curve 1). When added in solution 1 % acetic acid in the second experiment and in the third together with salt of alkaline metal ($NaNO_3$), which are possibly formed in underground water as natural surface active agents

(SAA), concentrations of Cu in these two experiments and Mn in the third experiment are apparently increased in 1.5 ~ 17.5 times (Fig. 5, curves 2, 3). The obtained results indicate that the heavy metals Cu and Mn can be transported in the capillary model, no matter how they are in the mobile forms of anions or cations and that the transport effect is influenced by organic substances and solution ionic content, as was supported by the results of the work[18].

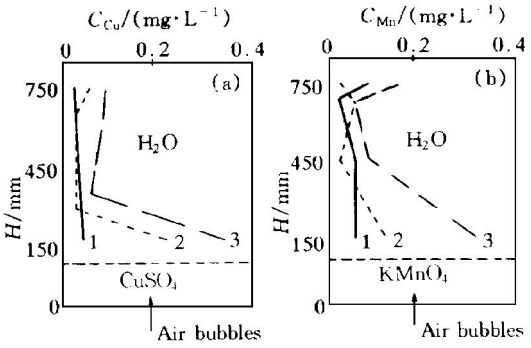

Fig.5 Concentration distribution of copper (a) and manganese (b) along tube of capillary model

1 — Without surface active agents (SAA);
2 — With SAA of 1 % solution of acetic acid;
3 — With SAA of 1 % solution of acetic acid and sodium nitrate
(a) — $CuSO_4$, 800 mg/L of Cu;
(b) — $KMnO_4$, 700 mg/L of Mn

In the second series of experiments, a tube (30 mm in diameter, 300 mm in height) with quartz particles (1 ~ 5 mm in diameter) and distilled water is used to simulate the porous medium. A layer of solution of $UO_2(NO_3)_2$ (40 mg/L) as the source of metal uranium and sometimes with fulvic acid FA (100 mg/L) as the underground organic substances is situated in the bottom of the tube. As in the first series of experiments a flow of air bubbles is fed in from the bottom. Analysis of solution samples is made by laser-luminescence method with device ANGARA (with a sensitivity 10^{-11} g/L for uranium).

From Fig. 6 it can be seen that along the tube the concentration of uranium decreases until it is raised by the surface of water in the tube, and that the concentration of uranium on the surface of water increases with time. The minimum of concentration means that the transported uranium dissipates in the process of penetration through the porous medium and then accumulates by the surface of porous medium. In comparison of diffusion another experiment without gas bubbles in the porous medium was conducted and the contribution of diffusion proved to be so small that can be neglected (see Fig. 6). A series of experiments have shown that the adsorption of $(UO_2)^{2+}$ by porous particles in the solution with FA is less than that without FA, the concentration of uranium, transported by the gas bubbles, however, is greater than that without FA. This demonstrates the significant contribution of dissolved organic substances to the formation of jet halos.

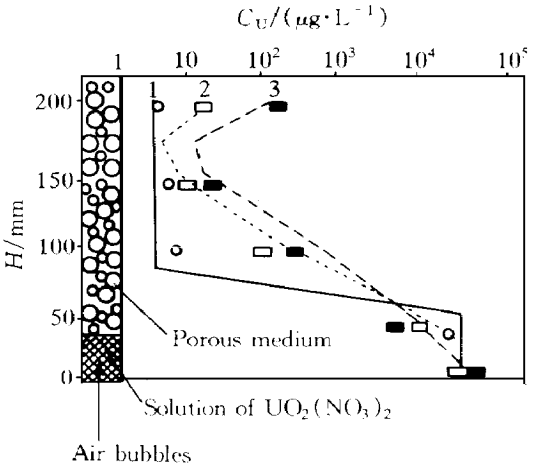

Fig.6 Concentration distribution of uranium and comparison of exmperimental data with numerical solution

1 — Initial model; 2 — in 30 min; 3 — in 120 min
○ — Contribution of diffusion in 120 min
□ — in 30 min; ■ — in 120 min

Comparison of the experimental results with the numerical solutions (Fig. 6) by Eqns. (5) and (6) gives physicochemical parameters: $V_{eff} = 4 \times 10^{-6}$ m/s, $D = 10^{-7}$ m^2/s, $C_0 = 35$ mg/L, $q_{max} = 0.5$ mg/m^3 (at $t = 30$ min) and q_{max} =

15 mg/ m^3 (at t = 120 min), $\beta = 2 \times 10^{-5}$ m^3/s and $\chi = 7 \times 10^{-7}$ m/s, which confirm the laboratory conditions. Therefore, to some degree, the proposed mathematical model may be used to predict the process and fate of transport of elements in the lithosphere in geological history.

5 CONCLUSIONS

(1) A physicochemical model of gas bubble facilitated transport of mobile forms of occurrence of metals has been established;

(2) The corresponding mathematical model is represented in a nonlinear integrodifferential quasiconvective equation;

(3) A partially implicit scheme of finite difference method is proposed and utilized for solving the nonlinear integrodifferential equation by means of iteration procedure;

(4) A stabilization effect of concentration front at stabilized speed V_s is determined by numerical solution;

(5) Physicochemical modeling with solutions of Cu, Mn and U under laboratory conditions has testified the numerical solution of the quasiconvective equation.

REFERENCES

1 Hitarov N I, Kravtsov A N, Voitov G I *et al*. Soviet Geology, (in Russian), 1979, (2): 62 - 73.

2 Wang Xianbin. Kexue Tongbao, (in Chinese), 1982, 27(17): 1069 - 1071.

3 Malmqvist L and Kristionsson K. Earth and Planetary Science Letters, 1994, 70: 407 - 416.

4 Krchmar B *et al*. Sb Geol Ved Uzita Geofyz, 1983, 18: 191 - 205.

5 Kristiansson K and Malmgvist L. Geoexploration, 1986, 24: 517 - 534.

6 Krchmar B. Praha, 1988, 25: 191 - 205.

7 Dukhanin A S. In: Abstracts of the Second All-union Conference for the Inorganic Gas Analysis, (in Russion), Leningrad, 1990: 255 - 256.

8 Ryss Yu S, Goldberg I S, Alekseev S G *et al*. Reports of Academy of Sciences of the USSR, (in Russian), 1987, 297(4): 956 - 958.

9 Putikov O F. Theoretical Basis of the Geoelectrochemical Exploration Methods, (in Russian). Leningrad: Leningrad State University Press, 1987: 158 - 165.

10 Govett C J S. and Atherden P L. Journal of Geochemical Exploration, 1987, 28: 201 - 218.

11 Dukhanin A S, Ryss Yu S and Voroshilov N A. Transactions of Russian Higher Education (Geology and Prospecting), (in Russian), 1989, (3): 53 - 61.

12 Putikov O F and Dukhanin A S. Reports of the Russian Academy of Sciences, (in Russian), 1994, 338 (2): 219 - 221.

13 Alekseev S G, Dukhanin A S, Veshev S A *et al*. Journal of Geochemical Exploration, 1996, 56(1): 79 - 86.

14 Wen Baihong. In: Abstracts of the All-Russian Science and Practice Conference of Young Scientists and Specialists, (in Russian). St Petersburg, 1997: 44 - 45.

15 Putikov O F and Wen Baihong. In: Abstracts of International Geophysical Conference Moscow' 97, Moscow, 1997, G2 - 8.

16 Putikov O F, Dukhanin A S and Mashijanov N R. Russian Geophysical Journal, (in Russian), 1994, (2): 5 - 10.

17 Wen Baihong. In: Abstracts of the Annual Science Conference of the Young Scientists of St. Petersburg State Mining Institute, (in Russian). St Petersburg, 1997, 4.

18 Wan Jiamin and Wilson J L. Water Resources Research, 1994, 30(1): 11 - 23.

(Edited by He Xuefeng)