

**ON THE HYDROTHERMAL TRANSPORT OF PALLADIUM (EXPERIMENTAL DATA)****Baranova N.N.** (GEOKHI RAS), **Tagirov B.R.** (IGEM RAS), **Kartashova L.F.** (IGEM RAS)

tagir@igem.ru, fax:(495) 951-15-87, tel.: (495) 230-82-31

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Palladium is one of elements related to platinum group. The experimental study of Pd-Cl-S-O-H system is actual according to the following items: 1) The estimates of Pd transport physico-chemical conditions in hydrothermal solutions; 2) The development of thermodynamical value system for aqueous solution species which could serve as database for modeling of Pt ore hydrothermal deposit formation. Three series of runs were performed; 1) Pd<sub>met</sub> solubility in aqueous and NaOH solutions at 400°C and 1 kbar; 2) Pd<sub>met</sub> solubility in acidic chloride solutions at same P-T parameters; 3) PdS (vysotskite) solubility in H<sub>2</sub>S solutions at 5-200°C within the broad range of pH values. The runs of 1-th and 2-nd series were carried out in titanium autoclaves treated by 20% HNO<sub>3</sub>. It was established that Pd<sub>met</sub> solubility in near neutral and weak alkaline solutions in the absence of complex-forming ligands is below the detectivity limit (0,1 ppb) Thus all subsequent runs were performed by use of solutions saturated in relation to the atmospheric oxygen, or in some cases by in introduction of 30-110 mg of 30% H<sub>2</sub>O<sub>2</sub>. It was found that the dissolved Pd concentration is stable within the broad range of pH values as a result of Pd(OH)<sub>2</sub> domination. The increase of Pd concentration is observed at pH >8.5 being responsible for Pd(OH)<sub>3</sub><sup>-</sup> formation.

The hydroxide Pd complex formation reaction constants were calculated as following: log K(Pd(OH)<sub>2</sub>) = -20,15 and log K(Pd(OH)<sub>3</sub><sup>-</sup>) = -18,22. Pd<sub>met</sub> solubility in acidic chloride solutions was studied at 400°C and P=300 – 1000 bar in equilibrium with oxygen fugacity buffers Cu<sub>2</sub>O/CuO, Cu/Cu<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> and Ni/NiO.

The distinct permeability of Pd<sub>met</sub> in relation to hydrogen allowed to use the sealed Pd ampoules as hermetic containers for the buffer location and their isolation from the experimental solution. Such technique assures the production of reliable experimental data.

We established that dissolved Pd in the equilibrium with Ni/NiO and Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> (reduced conditions) exists in a form of PdCl<sub>4</sub><sup>2-</sup> species. The formation reaction constant was calculated as Pd solubility at the presence of Cu<sub>2</sub>O/CuO buffer (oxidation conditions) was found to increase sufficiently presumably at the expense of oxidized Pd form (Pd IV).

The solubility of PdS (vysotskite) was experimentally studied in H<sub>2</sub>S saturated solutions (after the atmospheric oxygen was removed by argon flux) at T=5-60°C by use of ampoule technique. Similar experiments were performed at 200°C and pH =2.1-9.6 in autoclaves. pH values were produced by adding of 1m or 0,1m HCl. It was found that the PdS solubility in acidic solutions is not depending from pH; in weak acidic and near neutral conditions it increases having the peak at pH = pK<sub>1</sub>(H<sub>2</sub>S) which is characteristic for the Pd(HS)<sub>2</sub><sup>0</sup> and Pd(HS)<sub>3</sub><sup>-</sup> complex domination.

The common tendency of the temperature dependence of reaction constants was observed: their values decrease with the temperature increase. This phenomenon results in the PdS solubility decrease being mostly distinctive with in the acidic conditions (up to 10<sup>-9</sup>m). Third type of Pd complex, PdS(HS)<sub>2</sub><sup>2-</sup>, was established in alkaline solutions. Its formation reaction constant as well as PdS solubility is also decreasing with the temperature increase. The experimental studies demonstrated that the contribution of Pd hydroxide complexes in chloride – sulfide hydrothermal solutions is rather remarkable only in high alkaline conditions; along with this the role of Pd hydrosulfide complexes is sufficiently diminished with the temperature increase. Thus the Pd chloride complex, PdCl<sub>4</sub><sup>2-</sup>, is considered to exist as a predominant Pd species in chloride – sulfide hydrothermal solutions.

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