
NATURAL HYDROPHOBICITY AND FLOTATION OF SILVER-BEARING NATIVE GOLD

ĞÜMÜŐ İÇEREN NABİT ALTININ DOĐAL HİDROFOBİKLİĐİ VE FLOTASYONU

B. YARARC)
B.S. AKSOY(**)
I. BAYRAKTAR****)

ÖZET

Meksika'dan elde edilen, gümüş içeren, tabakalı yapıda nabit altının doğal olarak hidrofobik olduğu ve flotasyonu için reaktif gerekmediği saptanmıştır.

Konvensiyonel altın flotasyonu toplayıcıları olan ksantatların hidrokarbon zincirlerinin (etil, isopropil, isabutıl ve amil) etkileri araştırılmış ve ksantat türlerinin altın flotasyonunda önemli bir rolü olmadığı bulunmuştur.

Bu bildiri de nabit altının doğal olarak hidrofobik olduğu, yüzeyinin pürüzlü oluşunun hidrofobikliği azalttığı; demir ve kükük asitin altın yüzeylerine fiziksel olarak soğurulduğunu ve bunun hava kabarcığının yüzeye bağlanmasına karşı mekanik bir engel oluşturduğunu; ve sülfür iyonu konsantrasyonunun 10^{-5} M'dan büyük olması halinde sülfür iyonunun bir bastıncı olduğu, düşük konsantrasyonlarda ise ($< 10^{-5}$ M) canlandırıcı etki yaptığı deneysel olarak kanıtlanmıştır.

ABSTRACT

It was established that native gold flakes which contain silver, obtained from Mexico are naturally hydrophobic and require no reagents for flotation.

The role of conventional gold flotation reagents such as xanthates was also investigated and the effects of hydrocarbon chain in the series ethyl, isopropyl, isobutyl and amyl was found to be insignificant.

In this paper we demonstrate that native gold is inherently hydrophobic; that surface roughness reduces this hydrophobicity; that iron and hamic acids act as depressants by physical adsorption which creates a mechanical barrier between gold surface and air bubbles; and that sulfide ions act as hydrophobicity depressants at concentration of $C > 10^{-5}$ M, but have activator effects at $C < 10^{-5}$ M.

concentration of $C > 10^{-5}$ M, but have activator effects at $C < 10^{-5}$ M.

INTRODUCTION

The choice of method for concentration of gold-bearing materials depends on the mode of occurrence of gold such as in sulfide minerals, as tellurides, or in free form, etc. Numerous apphcational terms have evolved in this context and they refer to telluride gold, pyntic gold, carbonaceous gold, native gold, free-milling gold, etc. (1).

* : Professor of Metallurgical Engineering
** : Formerly Graduate Student at CSM
*** : Dr. Eng., Demir Export, Ankara

On the other hand, the processes chosen for concentration of values depend on the mode of occurrence, the degree of liberation and generally on the physico-chemical properties of the ores treated [2]. For example, while flotation-concentration is suitable at sizes smaller than 65 mesh (-200/μm), gravity separation operates best at much larger particle sizes.

This paper concerns itself with the inherent hydrophobicity of native gold and its behavior in flotation systems.

The following common observations are relevant to our interest:

Observation 1: During the gravity separation-treatment of native gold, such as jigging, tabling, use of spirals and their modification or indeed simple hand-panning, one frequently observes that some of the gold grains escape as a thin surface layer on top of the water phase, that is, they "skin float". It is common practice to add surfactants (such as dishwashing liquid) to the crossflow water in a tabling operation for example, to minimize skin flotation-losses to tabling tails.

Observation 2: It is known that if native gold-containing run of mine ores also contain sulfide minerals such as pyrite for example, flotation by xanthates is hindered by the presence of S⁻ ions in the medium, and high pH is not conducive to high recoveries. Furthermore, tarnished gold, that is gold which has been contaminated with humic substances from the organic matter decay that occurs in the environment, or contamination by iron oxides gives lower flotation recovery in metallurgical plant practice.

Hypothesis: These cases suggest that gold behaves as a naturally hydrophobic material, like graphite or molybdenite, as cited in Observation 1 above. Noting that metals in general exhibit high energy surfaces, which should enhance hydrophilic properties, the natural hydrophobicity observed in gold needs to be elucidated in connection with its flotation-concentration. Furthermore, the role of iron oxides, sulfide ions and humic substances need to be established in the same connection.

Natural Hydrophobicity of Gold

The well-known Young-Dupre equation:

$$\gamma_{SG} - \gamma_{SL} = \gamma_{LG} \cos \theta$$

where γ_{SG} , γ_{SL} and γ_{LG} are the solid-gas, solid-liquid, and liquid-gas interfacial tensions respectively while θ is the equilibrium contact angle. Conditions are right, flotation occurs at $\theta > 0$, which correlates with the thermodynamic flotation condition.

Using this concept, it is possible to plot contact angles against solution surface tension which usually produces a line as shown in Figure 1. This figure indicates that for a material that exhibits hydrophobicity in water, hydrophilic properties, i.e., $\theta = 0$ can be produced if the surface tension of the solution it contacts is reduced by some means such as using methanol or acetone-like substances which are completely water-miscible, or surfactants, all of which give low surface tension aqueous solutions. The low surface tension of the solution which leads to $\theta = 0$ or simply no flotation is known as the critical surface tension of wetting of this solid, γ_c [3].

From past experience we know that molybdenite, or graphite which would normally be considered naturally hydrophobic, and indeed float in water alone, do cease to adhere to air bubbles and thus not float in solutions that have surface tension values of 30 dyne/cm or smaller [4].

It needs to be noted here that the surface chemistry of the solid (mineral) is not altered by the use of low surface tension solutions cited above, and a conventional depressant-action-type mechanism need not be considered. What is relevant however, is that in a low-enough surface tension solution, the surface hydration film that exists on all surfaces and which can be stable (hydrophilic) or unstable (hydrophobic) is made less easy to break when a bubble collides with a hydrophilic solid particle in the flotation pulp [5].

Another point which needs to be observed in this connection is the fact that at solution surface tensions larger than that of the γ_c value, the material floats and at solution surface tension values equal to

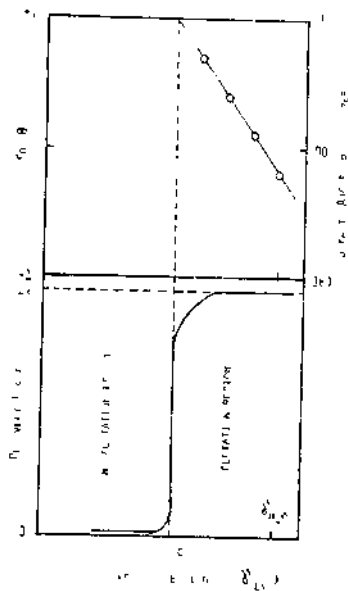


Figure 1: Correlation of critical surface tension of wetting, % and flotation. Top: γ_c as obtained by contact angle measurements. Bottom: γ_c as obtained by the Kacma-Yarar flotation method.

or smaller than the γ_c value, flotation does not occur. The relationship of the critical surface tension of a solid to its flotation behavior is also given in Figure 1.

EXPERIMENTAL

Degree of Hydrophobicity was determined by the "Bubble Pick Up Method", which is an established technique used in the optimization of flotation conditions when one has but a small sample of material [6,7].

The apparatus consisted of a glass tube from which a small bubble exits and is made to contact an immersed gold bed as shown in Figure 2. The hydrophobic particles which adhere to the bubble were picked up and counted or weighed. In the case of very fine particles, counting was made under a low magnification microscope.

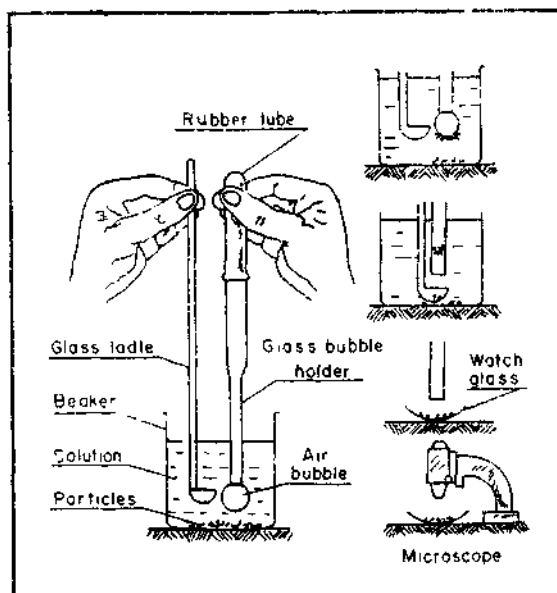


Figure 2: The bubble pick up method.

The main advantage of this method, is that mounting of a sample or polishing, which may lead to the alteration of "the natural state of its surface, as may indeed be necessary in contact angle measurements, is eliminated. The results are expressed as PI, pick-up index, i.e.:

$$PI = \left(\frac{P_n}{P} \right) 100$$

where :

- P_n - number of particles picked up under experimental conditions
- P - maximum number of particles picked up in a given set of tests

As compared to other small-scale laboratory techniques such as microflotation cells, or Hallimond tube or its modifications the method is fast, and becomes more reliable if the average of a number of pick-up tests is used for the calculation of PI.

It is also notable that as in the case of contact angle measurements, this technique gives data consistent within one set of experiments, and is best suited to distinguishing between no flotation, intermediate flotation and optimal flotation conditions. Correlating it with plant practice can only be accomplished by larger-scale tests.

The data reported in this paper were the arithmetic average of 10 experiments for each data point given.

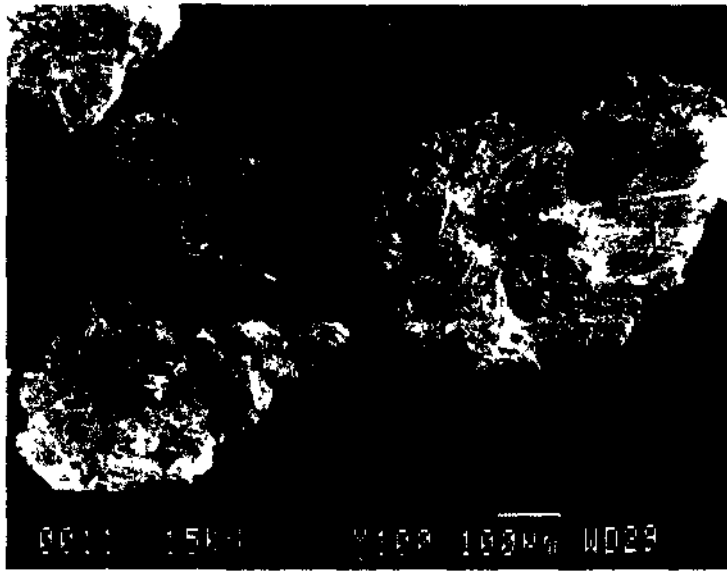
Contact Angle Measurements were made by a Rame-Hart contact angle goniometer, using the captive bubble and sessile drop methods. For this purpose, gold grains were melted into a bead at high temperature, and then hammered into a 5mm flake. A similarly prepared flake was rubbed on a 200 mesh sand paper to obtain a roughened surface for contact angle comparisons. Nitric acid cleaning was applied prior to measurements.

Chemicals used in all the experiments were "Analytical Grade" and water was distilled in an all-glass apparatus.

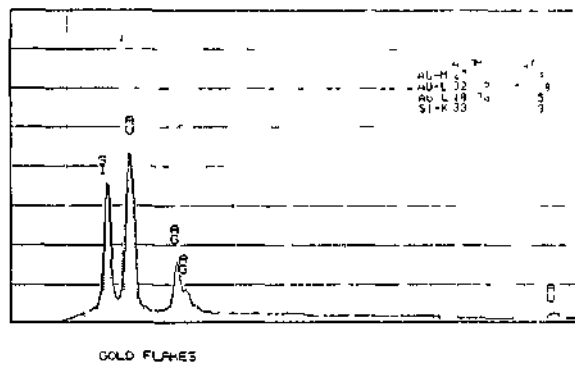
Xanthates used were the fractional recrystallization products of commercial samples, which were clear crystals. They were kept as solids under refrigeration and their solutions were prepared in the same day of usage.

The Gold Samples used in experimentation were placer samples obtained from Idaho, Mexico and Leadville, Colorado. They were subjected to concentration on a shaking table followed by superpanner. A final cleaning was carried out by hand-sorting under a 30X microscope.

All the data reported in this paper were obtained with the Mexico sample, and had the properties given in Figure 3. Particle sizes ranged between 75 and 200 micrometers and had the physical appearance shown in Figure 3.



(a)



(b)

Figure 3. Gold flakes used in this study. (a) Scanning electron micrograph and (b) EDS (Energy Dispersive X-Ray analysis) output of the grains.

Testing the Hypothesis that "Native Gold is Naturally Hydrophobic"

The curve given in Figure 4 indicates the critical surface tension of wetting of the gold sample used to be equal to about 40 dyne/cm. It is also worth remembering here that according to the discussion above, any material which exhibits a critical surface tension of wetting $\gamma_c < 70$ dyne/cm, the surface tension of water will float on its own without added reagents. Bubble pick up tests clearly show that the gold samples float in ordinary distilled water. The gold with which these experiments were conducted, was cleaned by nitric acid and also burned at about 700-800°C to eliminate all combustible, potential organic contaminants.

Literature data indicate that gold is indeed naturally hydrophobic [8,9]. In fact Bartell and Smith [10] report that both gold and silver exhibit low energy surfaces, and in the presence of oxygen-containing water, silver undergoes reactions which significantly alter the contact angle of water vapor condensed in it.

The Flotation Behavior of Native Gold in the Presence of Sulfide and Ferric Ions and Humic Acid

It was noted that native gold flakes are usually contaminated with iron oxides and organic decay products, generally known as "humic substances.". Furthermore, its surface is highly rough as noted in Figure 3. Gold surface is also usually heterogeneous; heterogeneity being generated by silver and silica-silicate inclusions, and at times iron oxides.

The roles of these structural and surface components in the flotation behavior of gold are discussed below.

Figure 5 shows the effect of ferric ions on the flotation of the native gold sample used, where it is seen that as the concentration of ferric ion increases in distilled water, observable hydrophobicity decreases. It can be shown by calculation that ferric ions are completely precipitated as ferric hydroxide $\text{Fe}(\text{OH})_3$ (hydrated iron oxide) at neutral pH. The adverse effect of Fe persists even in the presence of a xanthate collector.

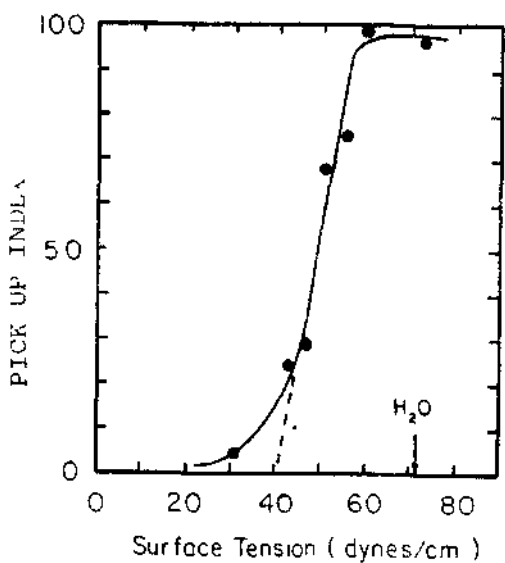


Figure 4. The critical surface tension of wetting of gold flakes. Solution surface tension arranged by methanol

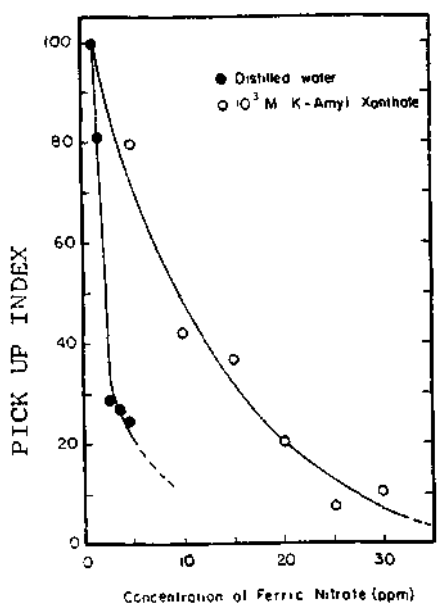


Figure 5: Effect of ferric Ion on the flotability of gold.

Further, If a sample that has shown zero flotability In the presence of Iron, Is washed thoroughly with distilled water and re-tested, It re-exhibits Its original natural hydrophobclty. This suggests that hydrated Iron oxides which are known to exist in colloidal-size fine particles are acting as a mechanical barrier between the air bubble and the hydrophobic surface; no chemical Interaction between the gold surface and Iron has taken place.

The same phenomenon Is observed, yet, to a smaller extent when humlc acid Is used, as can be seen In Figure 6. Humlc acids can be taken as low molecular weight multi-functional organic colloids. Their action In the depression of gold Is also physical, as In the case of Iron oxides and can be reversed by mere washing of the sample with distilled water.

The action of sulfide ions is a totally different phenomenon as can be seen In Figure's 7(a) and (b). Here we note that at very low concentrations of added Na²S (i.e., 10 M), sulfide ions act AS activators, namely, they enhance the flotability of our native gold sample. At higher than 10 M concentrations however, sulfide Is a depressant and Inhibits hydrophobclty at all concentrations even in xanthate-containing solutions.

If a freshly-ground pure pyrite sample Is treated with deoxygenated or oxygen-containing distilled water, filtered and the solution part tested for its effect on the hydrophobclty of gold, one notes that hydrophobclty is

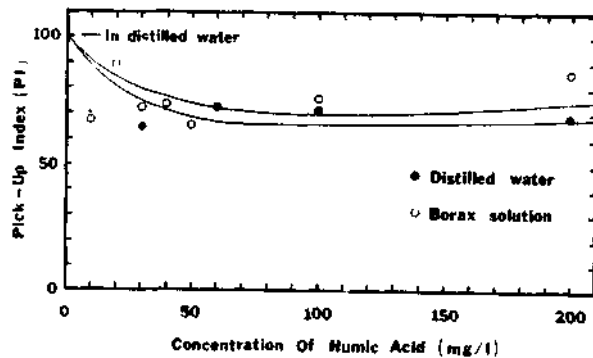


Figure 6: Effect of humlc acid on the flotability of gold.

completely depressed in such a solution. Chemical analyses show that such solutions contain high concentrations of dissolution products, of the order of 10^{-4} M and higher, derived from the Ionization and oxidation of pyrite.

Even if the gold sample is treated with xanthate ions and then treated with sulfide, its hydrophobicity is irreversibly Impaired by S^{2-} ions.

These data are in agreement with the findings of other investigators. For example, Walker et al [U], In electrochemical studies have observed the depressive action of sulfide species in the medium. The mechanism of such action is debated, however, It appears that the strong reducing action of sulfide ions in xanthate-containing media, and the strong chemical affinity of S^{2-} ions for metal surfaces Is playing an Important role in their depressant action.

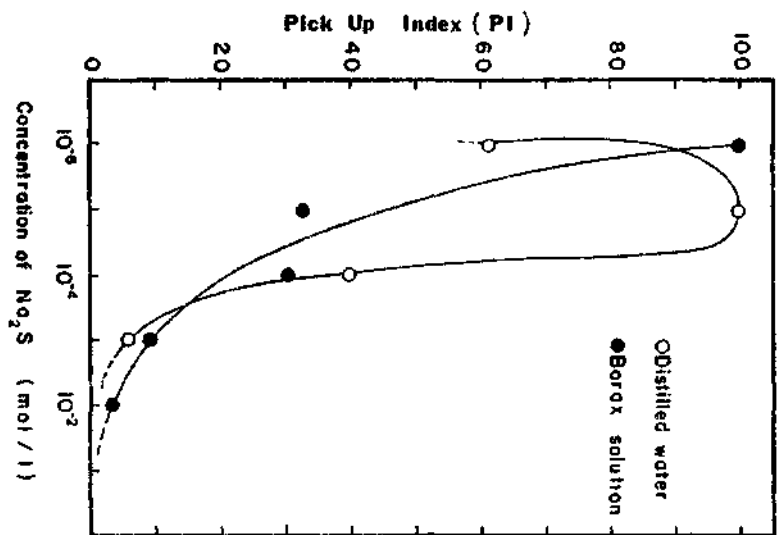
Role of pH and Ionic Strength

In the flotation-concentration of gold-bearing ores the pH of the medium varies in a wide range from as low as pH = 3 [12] to as high as pH = 10, the actual value being determined by the chemistry of the reagents used, the degree of oxidation of accompanying minerals and the chemical compositions of such minerals. Neutral pH is more commonly used for native gold recovery [13].

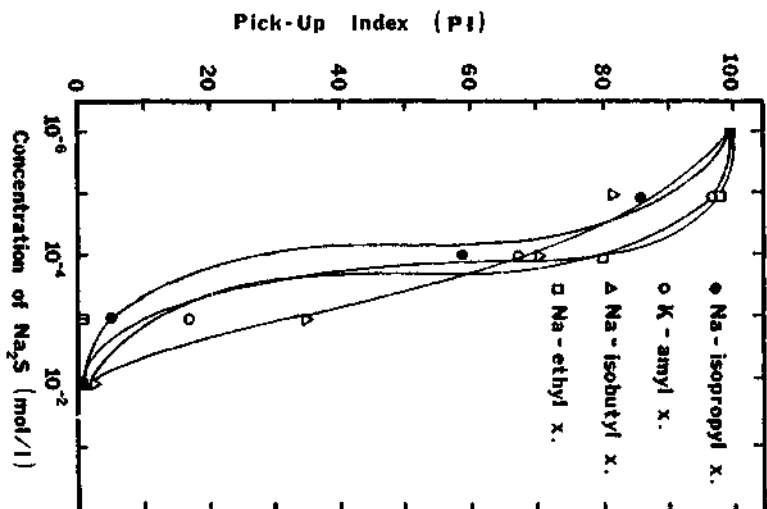
In the case of native gold flotability we find the following points to be significant:

Native gold shows maximum flotability In distilled water In the range pH = 6-9 the flotation being totally inhibited at pH > 10 as can be seen in Figure 8.

Figure 9 shows that if the ionic strength of the medium Is kept constant at $I = 10^{-2}$, gold shows relatively high natural hydrophobicity in the acid and neutral pH ranges, while high pH Is again deleterious. The role of roughness In this context is further discussed below.



(a)



(b)

Figure 7: Effect of Na_2S on the flotability of (a) Nascent gold, (b) gold, treated with xanthates.

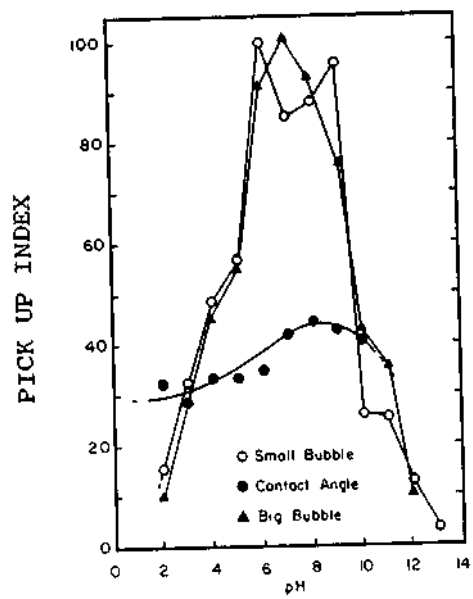


Figure 8: Effects of pH on the flotability and contact angle of gold.

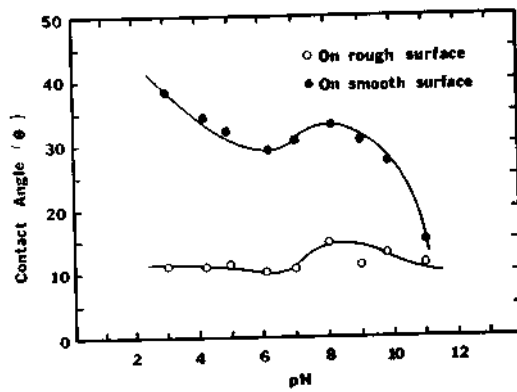


Figure 9: Effect of surface roughness on the relative degree of hydrophobicity of gold.

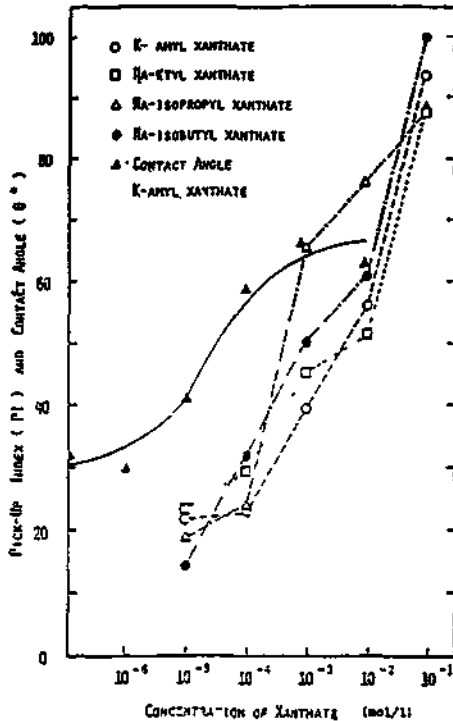


Figure 10: Effects of xanthates Cj to Cc concentrations on the hydrophobization of gold.

Role of Xanthate Structure in the Hydrophobization of Native Gold

Xanthates (or dithio carbonates) which have the general formula: R-O-CSS-M where: Me - a cation such as Na or K, and R - a hydrocarbon chain are commonly used as reagents in the flotation-concentration of gold ores. In most cases such ores used in metallurgical practice contain sulfides or tellurides alone or together with native gold grains.

In this study we have investigated the degree of hydrophobicity imparted to the gold sample studied by xanthates, without any other reagents such as activators or frothers.

Figure 10 shows the behavior of gold at various xanthate concentrations in borate buffer of pH - 9.2. The following are observed from this figure:

- 1) In borax solution, higher xanthate concentrations render native gold more hydrophobic.

2) The concentration-dependence of the effect of xanthates on the hydrophobization of gold is not a well-defined function of hydrocarbon chain structure If the xanthates are:

Aero-335, Sodium ethyl xanthate $C_2H_5-OCSS-Na$

Aero-343, Sodium Isopropyl xanthate: $C_3H_7-OCSS-Na$

Aero-317, Sodium isobutyl xanthate : $C^H_4-OCSS-Na$

Aero-350, Potassium amyl xanthate $C_5H_{11}^{OK}OCSS-Na$

At $C = 10^{-3}$ M the results show: Na-Isopropyl > Na-Isobutyl > Na-Ethyl > K-Amyl; at higher concentrations such as 0.1 M, the order is: Na-Isobutyl > K-Amyl > Na-Ethyl - Na-Isopropyl. We believe that the observed differences are within the limits of experimental error.

The flotation of native gold by xanthates is consistent with the findings of others [14] who report that high reagent concentrations produce more hydrophobicity and that dixanthogen, $(ROCSS)_n$, is the most likely entity responsible for it. Since dixanthogen is a neutral oil, one would expect it to be more readily-adsorbable on low-energy or naturally-hydrophobic solid surfaces which is the case with native gold.

Role of Roughness In the Flotability of Gold

A number of papers in the literature report electrochemical and contact angle measurement data on the native flotability of gold [8-11,13,14].

Figure 3 shows that the degree of roughness of native gold is much higher than one would expect in assumptions that gold flakes are smooth(H).

We have conducted a series of experiments seeking the relationship between the roughness of native gold surface and its flotation behavior. These data were also checked against an artificially prepared hydrophobic surface, by melting paraffin on a slide glass.

The highlights of our observations can be summarized as follows:

- 1) The native hydrophobicity of gold is hindered by the roughness of its surface. Namely, that if a gold flake is made smoother by sintering at elevated temperature, its hydrophobicity increases as indicated by increased contact angle measured under similar conditions to the ones obtained with rougher surfaces (see Figure 9).

- 2) Contact angle data obtained with paraffin surfaces and gold samples show the following patterns:
 - a) If $\theta < 90$, increase in roughness affects the hydrophobicity of the material in an adverse manner.
 - b) If $\theta > 90$, increase in roughness makes for a better flotation.

These data are in agreement with our findings reported above which noted that higher xanthate concentrations lead to better flotation of native gold and are also in agreement with the well-known Wenzel equation, i.e.,:

$$(\text{Roughness}) (\cos \theta_{\text{true}}) = (\cos \theta_{\text{measured}})$$

CONCLUSIONS

Based on this study we reach the following conclusions:

- 1) Native placer gold flakes are made highly heterogenous by inclusions of silver and silica plus silicates.
- 2) Such flake surfaces are highly rough and exhibit pits, valleys and peaks which vary in depth and width, ranging from a fraction of a micron to 10 microns.
- 3) Such flakes are naturally hydrophobic and float readily with distilled water, even after potential organic contaminants are burned away by heating of the sample at 700-800° their critical surface tension of wetting being about 40 dyne/cm. Roughness reduces the natural hydrophobicity of gold grains.
- 4) Ferric ions and humic acids retard bubble-particle adhesion in a flotation system, by forming physical barriers between particles and bubbles.
- 5) While native gold flakes exhibit higher hydrophobicity at neutral pH, pH > 9 is deleterious to natural flotability.
- 6) Unexpectedly, sulfide ions, at low concentrations, such as $[\text{Na}_2\text{S}] < 10^{-5}$ M act as activators and as strong depressants at all higher concentrations.

- 7) High concentrations of Cu-Cs-xanthates enhance the degree of hydrophobicity of native gold at all concentrations, the higher ones being preferable.
- 8) The heap leaching of gold is also influenced by the wetting phenomena which takes place at the cyanide solution-gold interface, and our findings in this connection will be presented in a separate publication.

REFERENCES

1. Taggart, A. F., "Handbook of Mineral Dressing", Wiley, N.Y., (1954), pp. 2-70 to 2-100.
2. Yarar, B. and Rao, S. R., "Flotation", in Encyclopedia of Chemical Processing and Design, J. J. McKetta (ed.), Marcel-Dekker, N.Y., (1985), vol. 23, pp. 454-508.
3. Yarar, B., "Gamma Flotation: A New Approach to Flotation Using Liquid-Vapor Surface Tension Control", In Annales, Proc. 2nd Latinamerican Flotation Congress, Concepcion, Chile, vol. 1, pp. C.2.1-C.2.30.
4. Kaoma, J. and Yarar, B., "Correlation of the Critical Surface Tension of Wetting and the Non-Stoichiometric Composition of Molybdenum Sulfide", in Proc. 4th Intl. Conf. on Chemistry and Uses of Molybdenum, H. F. Barry and H. Mitchell (eds.), Climax, Ann Arbor, Michigan, (1982), pp. 117-122.
5. Yarar, B., "Correlation of the Zeta-Potential and Flotability of Weathered Coal", SME-AIME Transactions, vol. 272, pp. 1978-1983, (1983).
6. Sun, S. C. and Troxell, R. C., "Try Bubble-Pickup for Rapid Flotation Testing", E&MJ, vol. 158(7), p. 79, (1957).
7. Lee, A. F., "A New Bubble Pick Up Technique As A Rapid Flotation Test Method", (discussion of), J. South Africa Inst. Min. Met., (November 1970), pp. 77-85.
8. White, M. L., J. Phys. Chem., vol. 68(10), pp. 3083-3085, (1964).
9. Erb, R. A., "Wettability of Metals Under Continuous Condensing Conditions", J. Phys. Chem., vol. 69(4), pp. 1306-1309, (1965).
10. Bartell, F. E. and Smith, J. T., "Alteration of Surface Properties of Gold and Silver As Indicated By Contact Angle Measurements", Ibid., vol. 57, pp. 165-172, (1953).

11. Walker, G. W., Walters, C. P., and Richardson, P. E., "Hydrophobic Effects of Sulfur and Xanthate on Metal and Mineral Surfaces", Intl. J. Min. Proc, vol. 18, pp. 119-137, (1986).
12. Yarar, B. and Pine, G. L., "Gold Content of Arizona Cinder Cones", paper prepared for presentation at Symposium on Precious and Rare Metals, Albuquerque, New Mexico, (April 6-8, 1988).
13. Wang, W. and Poling, G. W., "Methods for Recovering Fine Placer Gold", CIM Bull., vol. 76, pp. 47-56, (1983).
14. Miller, J. D., Misra, M., and Gopalakrishnan, S., "Fine Gold Flotation from the Colorado River Sand with the Air-Sparged-Cyclone", Preprint No. 85-397, SMA-AIME Fall Meeting, Albuquerque, New Mexico, (1985).
15. Gardner, J. R. and Woods, R., "An Electrochemical Investigation of Contact Angle and Flotation In the Presence of Alkylxanthate: Parti -Platinum and Gold Surfaces", Aust. J. Chem., vol. 27, pp. 2139-2148, (1974).