

**Molecular Dynamics Simulations of Metal-Cyanide Complexes: Fundamental Considerations in Gold Hydrometallurgy**Xihui Yin<sup>1</sup>, Aleksandra Opara<sup>1</sup>, Hao Du<sup>2</sup>, Jan D. Miller<sup>1</sup><sup>1</sup>Department of Metallurgical Engineering

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**Abstract**

This study utilizes molecular dynamics simulations (MDS) in order to evaluate the hydration state and the characteristics of metal-cyanide anions in aqueous solutions. Cyanide complexes of gold, silver, zinc, mercury, and copper were examined. Tetracyano anions of zinc and mercury showed the highest level of hydration, whereas dicyano anions of mercury, gold, and silver showed the lowest level of hydration. Several of the cyano anions were found to form clusters in solution. Other species, especially the tetracyano complexes, were found to be well dispersed in water.

This MDS information on the behavior of metal-cyanide complex anions may lead to further advances in the understanding of processes being used in gold hydrometallurgy operations. This paper discusses the results from simulations and how these results contribute

to a fundamental understanding of carbon adsorption, solvent extraction/ion exchange, and membrane water treatment processes.

**Keywords:** Metal-cyanide complex, MDS, hydration state

## 1. Introduction

Cyanide leaching coupled with carbon adsorption is the most popular method for gold recovery from low grade ores. Other less common gold recovery techniques include solvent extraction and ion-exchange. These methods exhibit significant selectivity for the aurocyanide anion but the reaction mechanisms associated with these processes have not been completely understood. Many mechanisms have been postulated for gold adsorption by activated carbon including:  $\text{Au}(\text{CN})_2^-$  anion exchange, precipitation of insoluble  $\text{AuCN}$ , pore reduction to elemental gold, or cluster formation (Mooiman et al., 1984). Now it seems that the adsorption reaction is most appropriately described by the adsorption of ion pairs at defects and cavities of the porous activated carbon structure. In the case of solvent extraction and ion-exchange, selective extraction of gold has been reported with neutral extractants and resins. The selectivity for gold from cyanide solution in both adsorption and solvent extraction/ion exchange seems to be due to the size to charge ratio, with lower charged and larger cyano anions being favored over other anions (Sole, 2008). This situation can be explained based on the hydration characteristics of the cyanide anions (Akser et al., 1986). It has been proposed that  $\text{Au}(\text{CN})_2^-$  anions have a low level of hydration which, in certain cases, enables selective adsorption/extraction (Wan and Miller, 1990).

Cyanide leach solutions contain, besides the aurocyanide anions, numerous other metal-cyanide anions. Despite the obvious significance of complex cyanide anions in cyanidation practice, fundamental knowledge of their behavior has not been completely established, as mentioned twenty years ago (Mooiman and Miller, 1991). The hydration characteristics of various metal-cyanide complexes is an important fundamental issue in gold

cyanidation operations and its understanding could potentially lead to advances in adsorption/extraction technology and membrane separation processes. For example, knowledge of the interaction of metal-cyanide anions in aqueous solutions (i.e. whether they are well dispersed or form clusters) could contribute to a better understanding of, and improvements in, processing technology.

Experimental study of the hydration of metal cyanide complex anions is difficult to be accomplished with vibrational spectroscopy. Molecular dynamics simulations (MDS) can complement such spectroscopic analysis, allowing for a description of the dynamic behavior of selected species (Allen, 2004). Molecular dynamics simulations of eight metal cyanide complexes which are commonly present in gold leach solutions were performed. Chosen metals of interest included precious metals (gold and silver) and heavy metals (mercury, zinc, and copper). Analysis of the simulation results focused on the hydration state and interaction of the complexes. The hydration state analysis included both structural properties and dynamic properties.

## 2. Methods

Molecular dynamics simulations were performed using the Amber 9 suite of programs (Case et al., 2005). For each type of cyanide complex, a simple cubic cell containing water molecules and metal cyanide complex anions together with potassium counter ions was constructed with a periodic condition. The extended simple point charge (SPC/E) water model was used to describe the water interactions.

The pair potential force field used in the simulations is given as a combination of the Lennard-Jones and the Coulomb electrostatic interactions, and can be expressed as:

$$U_{pair} = \sum_i \sum_j \left( 4\epsilon \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right) \quad (1)$$

where  $\epsilon$  is the energy parameter,  $\sigma$  is the size parameter,  $q$  is the charge, and  $r$  is the distance between species  $i$  and  $j$ . Ab initio simulation which is based on quantum chemistry was performed using the Gauss 03 simulation package in order to obtain optimized cyanide complex

structure as well as atomic charges. MP2 level (Møller–Plesset perturbation theory of the second order ) ab initio simulation employing 3-21G basis sets were utilized to create molecular orbitals for C and N, and SDD basis sets were used for metal atoms including Au, Ag, Hg, Cu, and Zn. During the simulation, the whole metal cyanide complex ion was simulated by structural optimization from which the bond length and bond angle can be obtained, and the complex is allowed to fluctuate during the entire simulation until energy is converged. The structures of each cyanide complex which is shown in Table 1 was compared with that reported in the literature(Sharpe, 1976), and good agreement was achieved regarding the bond lengths and angles between atoms, suggesting that low energy state structures of the complexes were obtained from the simulation. Also, the Mulliken atomic charges of each atom were obtained from ab initio simulation and used for further molecular dynamics simulations. The Lennard-Jones size and energy parameters were referenced from the literature (Heinz et al., 2008; Kotdawala et al., 2008; Mousazadeh and Marageh, 2006) and are given in Table 1. Finally, Lorentz-Berthelot mixing rules were applied to calculate the potential parameters of pairs (Allen and Tildesley, 1987; Du and Miller, 2007; Du et al., 2007):

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (2)$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (3)$$

In the analysis of the hydration state, a single metal cyanide ion and potassium counter ion were introduced into the box containing 1000 water molecules. The system was simulated for 1.5 ns including an equilibration time of 500 ps under NPT ensemble (constant moles, pressure and temperature) with pressure fixed at 0.1 MPa and the temperature fixed at 298 K, with the step size of 1 fs. The results were analyzed based on the simulation after equilibration ( $10^6$  steps of 1fs) under NVT ensemble (constant moles, volume and temperature).

In other simulations, to examine interactions of the metal cyanide complexes, simple cubic cells containing 1000 water molecules, 8 metal cyanide ions and potassium counter ions were constructed with periodic boundary conditions. In the initial configuration, water molecules and cyanide complexes were randomly distributed in the simulation cell. The charge

of the system was balanced by potassium counter ions. The system was simulated for 2 ns including an equilibration time of 1 ns under NPT ensemble with pressure fixed at 0.1 MPa and the temperature fixed at 298 K. Again the step size was 1 fs. The results were analyzed based on the last 1 ns in the simulation ( $10^6$  steps of 1 fs) under NVT ensemble.

**Table 1. Potential parameters for MDS**

Species	Atom	q [C]	$\epsilon$ [Kcal/mol]	$\sigma$ [Å]	Bond angle [degree]		bond length [Å]	
					C-Metal-C	Metal-C-N	C-Metal	C-N
<b>Au(CN)<sub>2</sub><sup>-</sup></b>	Au	0.016	5.29	2.95				
	C	0.107	0.1529	3.63	180	180	2.020	1.197
	N	-0.615	0.1748	3.2				
<b>Ag(CN)<sub>2</sub><sup>-</sup></b>	Ag	0.045	4.56	2.955				
	C	0.089	0.1529	3.63	180	180	2.058	1.198
	N	-0.611	0.1748	3.2				
<b>Hg(CN)<sub>3</sub><sup>-</sup></b>	Hg	0.561	3.13	3.3				
	C	0.076	0.1529	3.63	120	180	2.147	1.196
	N	-0.596	0.1748	3.2				
<b>Hg(CN)<sub>4</sub><sup>2-</sup></b>	Hg	0.337	3.13	3.3				
	C	0.100	0.1529	3.63	109	180	2.237	1.199
	N	-0.684	0.1748	3.2				
<b>Hg(CN)<sub>2</sub><sup>0</sup></b>	Hg	0.843	3.13	3.3				
	C	0.044	0.1529	3.63	180	180	2.025	1.194
	N	-0.465	0.1748	3.2				
<b>Cu(I)(CN)<sub>3</sub><sup>2-</sup></b>	Cu	0.276	4.72	2.616				
	C	-0.047	0.1529	3.63	120	180	1.835	1.203
	N	-0.712	0.1748	3.2				
<b>Cu(I)(CN)<sub>2</sub><sup>-</sup></b>	Cu	0.434	4.72	2.616				
	C	-0.122	0.1529	3.63	140.3	180	1.752	1.198
	N	-0.595	0.1748	3.2				
<b>Zn(CN)<sub>4</sub><sup>2-</sup></b>	Zn	0.852	4.82	2.651				
	C	-0.052	0.1529	3.63	109	180	2.024	1.197
	N	-0.654	0.1748	3.2				

### 3. Results and Discussion

#### 3.1. Hydration of metal-cyanide complexes

The radial distribution function (RDF) was constructed using the separation distance between the oxygen in water and the nitrogen of the cyanide complexes. As can be seen from Figure 1, as the RDF curves shift to the right, the distance between the water molecules and the cyanide complex increases.

#### Figure 1.

Additionally, the hydration number for cyanide nitrogen, defined by the first minimum of the RDF was calculated as (Sansone et al., 2000):

$$n(r) = 4\pi\rho \int_0^r g(r')r'^2 dr' \quad (4)$$

where  $\rho$  is the density of particles in the given volume. This hydration number for cyanide nitrogen refers to the average number of the nearest water molecules around the nitrogen atom in the metal cyanide complex in the first hydration shell. Each atom in the cyanide complexes has interaction with water molecules more or less. The interaction between nitrogen atoms in the cyanide complex and oxygen atoms from water molecules was selected, because the nitrogen atom has the most contact with water molecules, regardless of cyanide complex structures. Then, based on the hydration number for cyanide nitrogen, the hydration number for the cyanide complex can be estimated by considering the shape factor. The shape factor is calculated based on the number of ligands after the mathematical correction in which the overlap region of hydration shell of nitrogen is subtracted according to the geometric shape of cyanide complex. The hydration number for the cyanide complex is calculated by multiplying the hydration number for cyanide nitrogen by the shape factor. It should be noted that in this calculation, an approximation was used that the water molecules are homogeneously distributed in each hydration shell of the nitrogen atom. Table 2 shows the characteristic features of the RDFs and calculated hydration numbers for cyanide nitrogen and metal cyanide complexes. The resulting order of estimated hydration number for cyanide complex was found

to be as follows:  $\text{Zn}(\text{CN})_4^{2-} > \text{Hg}(\text{CN})_4^{2-} > \text{Cu}(\text{I})(\text{CN})_3^{2-} > \text{Hg}(\text{CN})_3^- > \text{Cu}(\text{I})(\text{CN})_2^- > \text{Ag}(\text{CN})_2^- > \text{Au}(\text{CN})_2^- > \text{Hg}(\text{CN})_2^0$ .

**Table 2.** Characteristic features of the radial distribution functions between cyanide nitrogen and water oxygen for different cyanide complexes. Also included are the hydration numbers for the cyanide nitrogen and the estimated hydration number for cyanide complexes.

Species	$r_{\max 1}$	$g_{\max 1}$	$r_{\min 1}$	$g_{\min 1}$	Hydration number for cyanide nitrogen	Shape factor	Estimated hydration number for cyanide complex
$\text{Zn}(\text{CN})_4^{2-}$	2.825	2.719	3.425	0.437	4.098	3.582	14.681
$\text{Hg}(\text{CN})_4^{2-}$	2.775	2.667	3.425	0.478	3.998	3.727	14.902
$\text{Cu}(\text{I})(\text{CN})_3^{2-}$	2.775	3.184	3.425	0.423	4.743	2.783	13.200
$\text{Hg}(\text{CN})_3^-$	2.825	2.225	3.425	0.636	3.576	2.898	10.336
$\text{Cu}(\text{I})(\text{CN})_2^-$	2.825	2.854	3.475	0.545	4.532	1.972	8.939
$\text{Ag}(\text{CN})_2^-$	2.825	2.389	3.375	0.613	3.838	1.998	7.669
$\text{Au}(\text{CN})_2^-$	2.825	2.249	3.425	0.644	3.767	1.995	7.513
$\text{Hg}(\text{CN})_2^0$	2.925	1.417	3.425	0.901	3.285	1.995	6.552

From the results of hydration number for cyanide complexes, it is clear that the two most important factors influencing the extent of hydration of metal-cyanide complexes are the charge and the number of ligands. Highly charged ions tend to have stronger interaction with water molecules and a larger hydration shell than the neutral molecules. As expected, the results also suggest that the hydration increases with an increase in the number of cyanide ligands. Finally, for equally charged species bound with the same number of cyanide ligands, the hydration order can be examined. The trend of the hydration state tends to follow the polarity of the element. For example, in the case of single-charged dicyano-complexes, the hydration number is  $\text{Cu}(\text{I}) > \text{Ag} > \text{Au}$ .

In order to get a better understanding of the dynamic behavior of water molecules around different metal cyanide complexes, the water residence time was analyzed as a function of distance to the center of mass of the cyanide ligands. The residence time  $\tau$  refers to the time

that a water molecule stays in a given hydration shell of cyanide complex. It is calculated using the correlation function,  $R(t)$  (Berendsen et al., 1987; Koneshan et al., 1998):

$$\tau = \int_0^{\infty} \langle R(t) \rangle dt \quad (5)$$

where  $R(t)$  is defined by

$$R(t) = \frac{1}{N_h} \sum_{i=1}^{N_h} [\theta_i(0)\theta_i(t)] \quad (6)$$

where  $\theta_i(t)$  is the Heaviside unit step function which has the value 1 if a water molecule is in the hydration shell at time  $t$  and zero otherwise.  $N_h$  is the number of water molecules in each layer.

As another indicator of hydration state, the residence times of water molecules in the first hydration shell of various cyanide complexes as a function of distance to the center of mass (COM) of the cyanide complexes were calculated. The residence times in the primary hydration shell as well as in the bulk are presented in Table 3. It is noted that the residence time in the primary water layer is always longer than the residence time in the bulk water, indicating the significance of the interaction between water molecules and metal cyanide complexes. The order for residence time in the primary hydration shell for different cyanide complexes is as follows:  $\text{Cu(I)(CN)}_3^{2-} > \text{Cu(I)(CN)}_2^- > \text{Zn(CN)}_4^{2-} > \text{Hg(CN)}_4^{2-} > \text{Hg(CN)}_3^- > \text{Ag(CN)}_2^- > \text{Au(CN)}_2^- > \text{Hg(CN)}_2^0$ . As an example, Figure 2 shows the residence time as a function of distance to the COM of  $\text{Cu(I)(CN)}_3^{2-}$  and  $\text{Hg(CN)}_2^0$  which have the largest and the smallest hydration number for cyanide nitrogen among all the cyanide complexes. Comparing the intensity of the first peak which refers to the residence time in the primary hydration shell, the results suggest that  $\text{Cu(I)(CN)}_3^{2-}$  has stronger interaction with water molecules than  $\text{Hg(CN)}_2^0$ . Generally, the residence time in the primary hydration shell follows a trend similar to the trend in the hydration number analysis.



**Table 3.** Comparison of primary water residence time for metal cyanide complexes with water residence time in the bulk solution and with the hydration number for the metal cyanide complexes.

Species	Residence time		Estimated hydration number for cyanide complex
	Primary water layer (ps)	Bulk water (ps)	Primary water layer
$\text{Cu(I)(CN)}_3^{2-}$	3.82	2.02	13.200
$\text{Cu(I)(CN)}_2^-$	3.77	2.10	8.939
$\text{Zn(CN)}_4^{2-}$	3.25	1.55	14.681
$\text{Hg(CN)}_4^{2-}$	3.17	1.61	14.902
$\text{Hg(CN)}_3^-$	2.89	1.88	10.336
$\text{Ag(CN)}_2^-$	2.65	1.78	7.669
$\text{Au(CN)}_2^-$	2.60	1.80	7.513
$\text{Hg(CN)}_2^0$	2.47	1.81	6.552

**Figure 2.**

### 3.2. Interaction of metal-cyanide complexes

In order to study the interaction between cyanide complexes, MDS were performed using eight metal cyanide complexes and potassium counter ions in a simulation box with 1000 water molecules. The results are presented in the following sections.

#### 3.2.1. Tetracyano complexes

Tetracyano anions of zinc and mercury were simulated (Figure 3). Both of these complexes exhibit similar behavior. They are well dispersed in water. Tetracyano anions considered in this study showed a strong hydration state due to the high charge and large number of ligands which enable them to have a larger hydration shell. This explains why they have little interaction and tend to be dispersed in aqueous solution.

### 3.2.2. Tricyano complexes

Molecular dynamics simulations of cuprous and mercury tricyano anions were performed. Even though they share the same molecular structure, copper and mercury tricyano complexes behave somewhat differently in water. As shown in Figure 4,  $\text{Hg}(\text{CN})_3^-$  ions tend to form clusters in aqueous solution and the cluster formed by  $\text{Hg}(\text{CN})_3^-$  is more stable than the cluster formed by  $\text{Cu}(\text{CN})_3^{2-}$ . It is also observed that the interaction between  $\text{Cu}(\text{CN})_3^{2-}$  ions is very weak and only unstable dimers are formed during the simulation. This may be due to its relatively strong hydration state. Since both tricyano complexes have the same molecular structure, it is expected that the difference in the interaction behavior is mainly attributed to the charge effect and polarity of the metal.

### 3.2.3. Dicyano complexes

Simulations of dicyano complexes of copper, gold, and silver were completed. Snapshots from simulations are given in Figure 5. All three dicyano complex ions form clusters at the equilibrium state. The formation of clusters of  $\text{Au}(\text{CN})_2^-$  and  $\text{Ag}(\text{CN})_2^-$  ions can be explained by the weak hydration state as presented in the previous section. The estimated hydration number for  $\text{Cu}(\text{CN})_2^-$  ions is only slightly greater than  $\text{Au}(\text{CN})_2^-$  and  $\text{Ag}(\text{CN})_2^-$ . The overall hydration state of  $\text{Cu}(\text{CN})_2^-$  is still relatively weak and cluster formation can be expected.

### 3.2.4. Neutral species

The behavior of the neutral cyanide species  $\text{Hg}(\text{CN})_2^0$  was simulated. The molecules form chain-like structures in water (Figure 6). As revealed by hydration number analysis and residence time analysis, neutral mercury cyanide molecules showed very low level of hydration in comparison with other cyanide species. This characteristic results in a strong tendency for aggregation.

**Figure 3.**

**Figure 4.**

Figure 5.

Figure 6.

#### 4. Gold Processing Chemistry

Many of the cyanidation processes used in gold hydrometallurgy plants can be examined with respect to the results from MDS. So far, the main approach to understand processes like activated carbon adsorption, solvent extraction/ion exchange, or membrane water treatment has been to measure the kinetics and/or equilibrium state of the system. This MDS study opens the way for a more comprehensive analysis, where the reaction details can now be based on the expected behavior of cyanide complexes in a certain environment. Ensuing discussion sections indicate how the MDS results from this study can complement our understanding of activated carbon adsorption/desorption, solvent extraction/ion exchange, and membrane water treatment processes.

##### 4.1. Activated Carbon Adsorption

Activated carbons present a variety of advantages over other gold recovery methods. Therefore, the mechanism of adsorption and the reason for selective adsorption from cyanide solutions are of interest. A better understanding of the adsorption reaction would lead to advances in activated carbon preparation and would enable an improved basis for the selection of the most suitable carbons (McDougall and Hancock, 1981).

It has been established that the order of carbon adsorption for the metal-cyanide complexes considered in this study is as follows (Marsden and House, 2006):



The only species directly competing with gold and silver cyanides for adsorption sites is the neutral mercury cyanide molecule  $\text{Hg}(\text{CN})_2^0$ .

One of the theories of activated carbon adsorption is based upon ionic size and hydration (Cho et al., 1979). It is assumed that aurocyanide ions are larger and have a smaller

hydration shell than other metal-cyanide ions and thus are selectively adsorbed by activated carbon. The MDS results on hydration show that  $\text{Au}(\text{CN})_2^-$  ions have a lower hydration state than many other metal-cyanide complexes and thus the low hydration state may be an important reason for gold selectivity over, for instance, silver in activated carbon adsorption from cyanide solution. Moreover, the neutral mercury cyanide molecules,  $\text{Hg}(\text{CN})_2^0$ , were found to have the lowest hydration number of all complexes considered in this study. That further supports the conclusion that the lower the hydration number of a metal-cyanide complex, the higher the carbon adsorption.

Moreover, the strong tendency of  $\text{Au}(\text{CN})_2^-$  to form stable clusters may increase the possibility of adsorption. The hydrophobic tendency of aurocyanide anions and their corresponding cluster formation probably contribute to the selectivity exhibited in ion pair adsorption by activated carbon. Similarly,  $\text{Ag}(\text{CN})_2^-$  ions also form clusters, although not as strongly as  $\text{Au}(\text{CN})_2^-$ . The phenomenon of aggregation may be of importance in the adsorption reaction and cluster formation may account for stabilization at the activated carbon surface.

#### 4.2. *Solvent Extraction and Ion Exchange*

Several types of organic solvents and ion exchange resins have been proposed as process alternatives to conventional carbon adsorption (Cho et al., 1979). They often offer higher selectivity than activated carbon.

One extractant group for the selective recovery of gold from cyanide solutions is the group of phosphorous extractants including alkyl phosphates, phosphonates, phosphinates and phosphine oxides, particularly the butyl derivatives. Tributyl phosphate (TBP) and dibutyl butyl phosphonate (DBBP) are good examples of phosphorous-containing species that have been examined for gold extraction. Research has demonstrated that TBP is capable of selective extraction of gold from cyanide solution and solvent extraction processes generating 99.99% purity of gold have been developed. Moreover, it is selective for gold over nickel, cobalt, iron, and zinc, but not so much for silver or copper (Marsden and House, 2006). Another group of organic solvents that can be used for gold extraction from cyanide solutions are modified amines. They also have been shown to be selective for gold, especially with the addition of TBP

as a modifier (Wan and Miller, 1990). At high cyanide concentrations, DBBP was found to selectively extract gold over mercury (Diaz et al., 1992) under conditions where gold was extracted as  $\text{Au}(\text{CN})_2^-$ , while mercury was present as  $\text{Hg}(\text{CN})_4^{2-}$ .

It has been suggested that the selectivity of such solvent extractants, as in the case of carbon adsorption, is due to size/charge effects and the hydration state of the cyanide complexes (Miller et al., 1985; Wan and Miller, 1990). As the hydrophobic character of the species increases, their affinity for the organic extractants increases, and they are removed from the aqueous phase. As mentioned previously, the MDS results indicate that the aurocyanide anion has one of the lowest hydration states of all common metal-cyanide complexes. On the other hand, the large mercury tetracyanide complex is well hydrated and thus the MDS results explain why mercury was not extracted by DBBP from alkaline cyanide solutions under appropriate conditions.

#### 4.3. *Membrane Water Treatment Processes*

Membrane technology has recently become utilized in the mining industry. It is most notably used in process water treatment, but new developments suggest that membranes could also be used to recover valuable species from leach solutions (Lien, 2008). Until recently, the selection of appropriate membranes for a given application was mostly based on empirical data, and not so much on fundamental information. In the best case scenario, size factors (such as the nominal pore size or the molecular weight cut-off) acted as a guide for membrane selection (Nunes and Peinemann, 2001).

Recent studies performed at the University of Utah show, however, that other factors may be of equal importance. Surface properties of a membrane, especially its hydrophobic character, significantly influence the separation of ionic species. Two flat-sheet ultrafiltration membranes, both having the same nominal pore size, were used in the filtration of various metal-cyanide complexes. From contact angle measurements, it was established that one of the membranes was extremely hydrophilic, while the other one was hydrophobic. Results showed that, while aurocyanide rejection with both membranes was zero, the hydrophobic membrane rejected other metal-cyanide ions whereas the hydrophilic membrane did not. The most visible

difference was obtained in the case of zinc and mercury cyanides, where the hydrophobic membrane showed more than 30% rejection of these metal complexes and the hydrophilic showed no rejection (Opara, 2010).

Such distinctive behavior of various metal-cyanide complexes during polymeric membrane filtration can be explained by their hydration state as revealed from MDS results. The aurocyanide anion is weakly hydrated, thus it will not be rejected by either the hydrophobic or hydrophilic membrane surface. Its rejection will be mostly based on the nominal pore size. On the other hand, other metal-cyanide ions, most notably tetracyano complexes of mercury and zinc, are well hydrated and their rejection will be dependent on the hydrophobicity of the membrane.

This fundamental knowledge of the hydration state of metal-cyanide complexes and the hydrophobicity of various polymeric membranes may lead to future advances in gold processing technology. Immediate separation of the pregnant solution into two streams of reduced volumes might be achieved. One stream would contain only weakly hydrated species, most importantly gold and silver cyanides, and could be sent for further hydrometallurgical processing. All well-hydrated ions would be kept in the second stream, which could be directly sent for wastewater treatment or recycled, providing additional cyanide for leaching.

## 5. Conclusions

This MDS study analyzes the hydration state (structure and dynamics) as well as the interactions of metal-cyanide anions in aqueous solutions. The hydration order with respect to estimated hydration number for cyanide complexes was found to be:  $\text{Zn}(\text{CN})_4^{2-} > \text{Hg}(\text{CN})_4^{2-} > \text{Cu}(\text{I})(\text{CN})_3^{2-} > \text{Hg}(\text{CN})_3^- > \text{Cu}(\text{I})(\text{CN})_2^- > \text{Ag}(\text{CN})_2^- > \text{Au}(\text{CN})_2^- > \text{Hg}(\text{CN})_2^0$ . The hydration order with respect to primary water residence time was found as  $\text{Cu}(\text{I})(\text{CN})_3^{2-} > \text{Cu}(\text{I})(\text{CN})_2^- > \text{Zn}(\text{CN})_4^{2-} > \text{Hg}(\text{CN})_4^{2-} > \text{Hg}(\text{CN})_3^- > \text{Ag}(\text{CN})_2^- > \text{Au}(\text{CN})_2^- > \text{Hg}(\text{CN})_2^0$  which is similar to the trend of hydration numbers for cyanide nitrogen. Tetracyano complexes are well hydrated, do not interact, and are well dispersed in water. On the other hand, aurocyanide and argentocyanide anions show a low hydration state and tend to form clusters in water. There does not seem to be any

correlation between hydration and whether the cyanide species are SAD/WAD; however, more species need to be studied.

This MDS description of metal-cyanide complexes provides a better understanding of the chemistry of gold cyanidation processes. Selectivity in gold recovery from cyanide solutions that has been discussed in the literature for a couple of decades can now be attributed with greater confidence to the lower hydration state of aurocyanide in comparison to other cyanide complexes. Moreover, aggregation of gold and silver cyanide anions into clusters may contribute to the selectivity of certain solution concentration and purification processes. Finally, it appears that the hydration characteristics of metal-cyanide complexes could be used as a basis for advances in membrane fractionation systems in the treatment of alkaline cyanide solutions.

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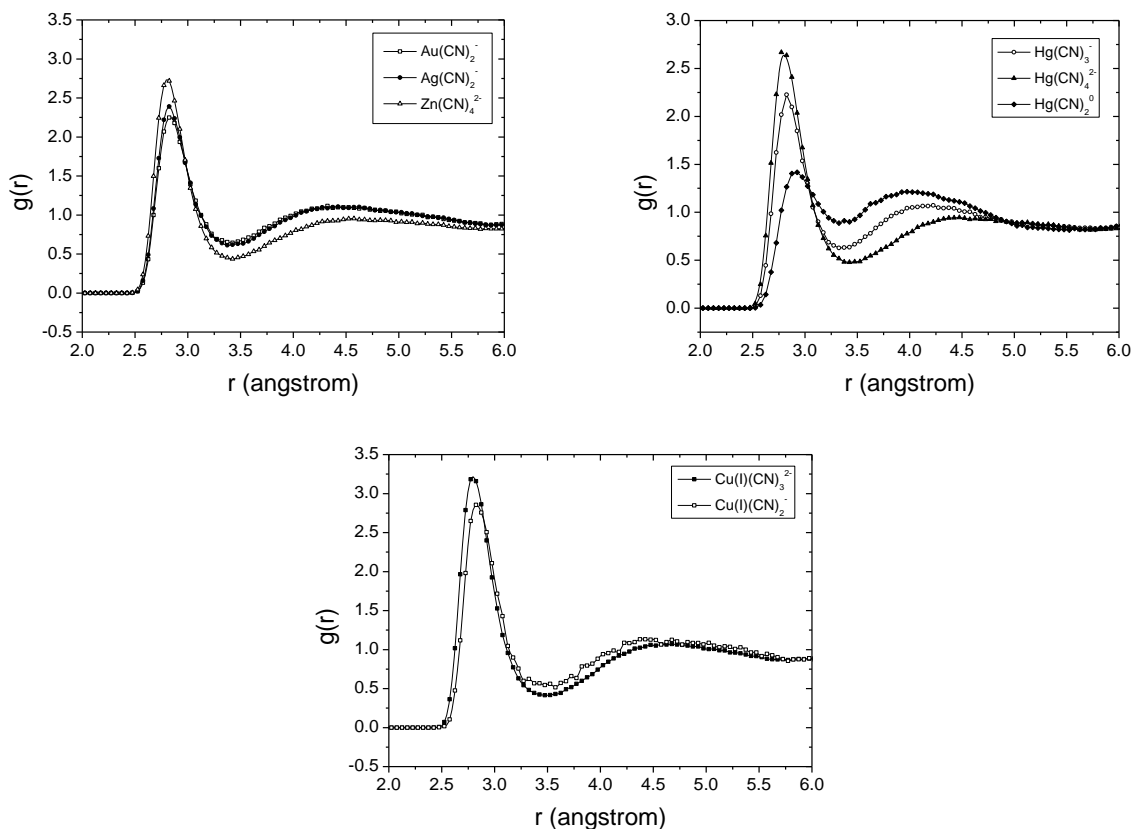
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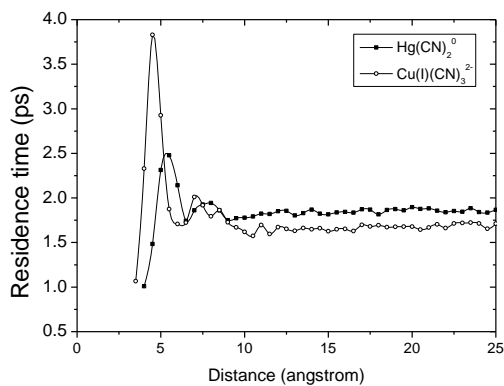
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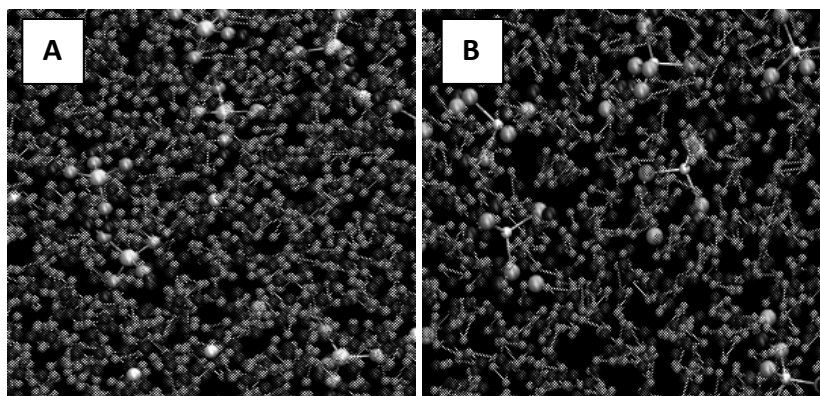
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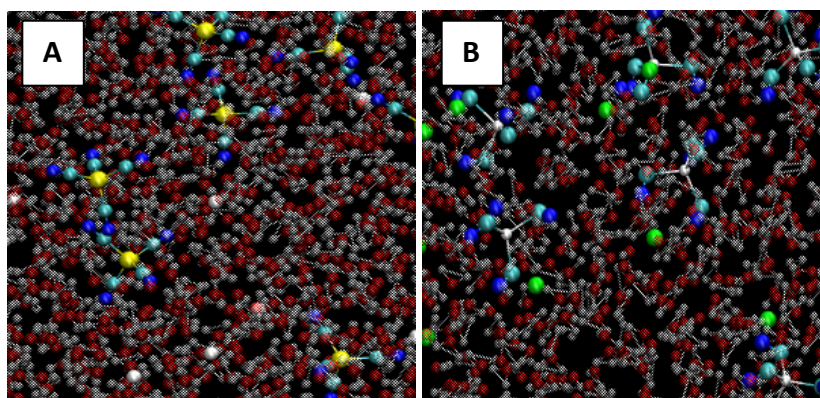
**Figure 1.** Radial distribution functions of selected metal-cyanide complexes and water.

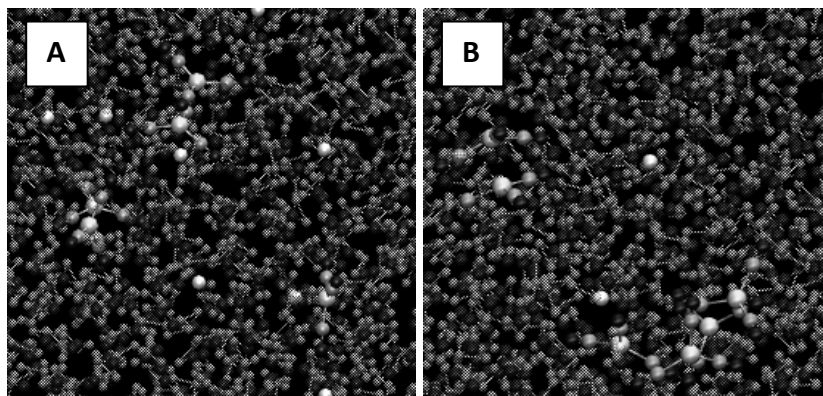


**Figure 2.** Comparison of water residence time for strongly hydrated ( $\text{Cu(I)(CN)}_3^{2-}$ ) and weakly hydrated cyanide ions ( $\text{Hg(CN)}_2^0$ ) as a function of distance to the center of mass of cyanide ions.

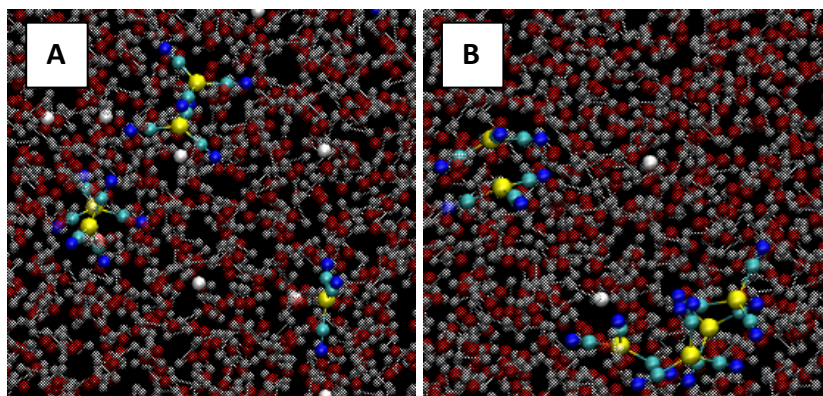


**Figure 3.** Snapshots from MDS of (A)  $\text{Zn}(\text{CN})_4^{2-}$ , and (B)  $\text{Hg}(\text{CN})_4^{2-}$ . Color codes for (A): blue-nitrogen, cyan-carbon, yellow-metal molecule (Zn), white-counter ion ( $\text{K}^+$ ). Color codes for (B): blue-nitrogen, cyan-carbon, white-metal molecule (Hg), green-counter ion ( $\text{K}^+$ ). (Color image can be viewed from the online version.)

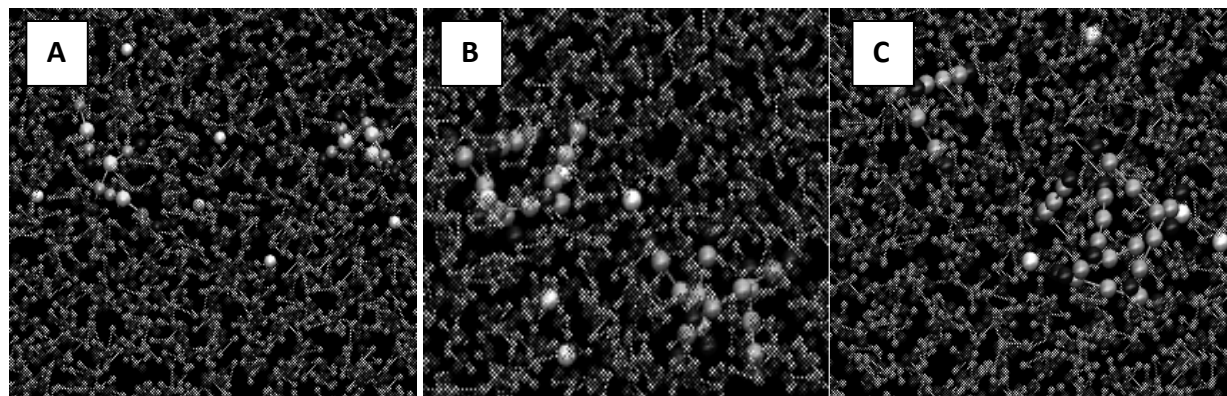




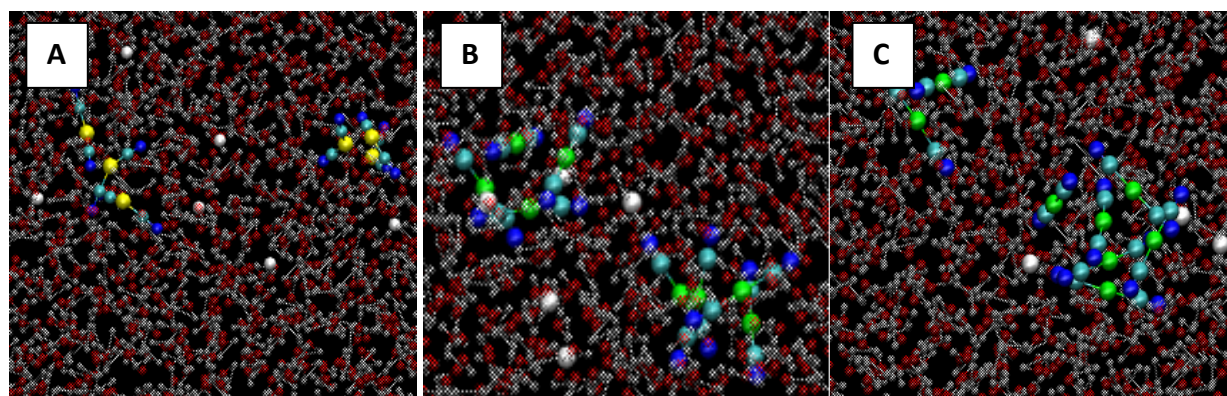
**Figure 4.** Snapshots from MDS of (A)  $\text{Cu(I)(CN)}_3^{2-}$  and (B)  $\text{Hg(CN)}_3^-$ . Color codes for (A): blue-nitrogen, cyan-carbon, yellow-metal molecule (Cu), white-counter ion ( $\text{K}^+$ ). Color codes for (B): blue-nitrogen, cyan-carbon, yellow-metal molecule (Hg), white-counter ion ( $\text{K}^+$ ). (Color image can be viewed from the online version.)

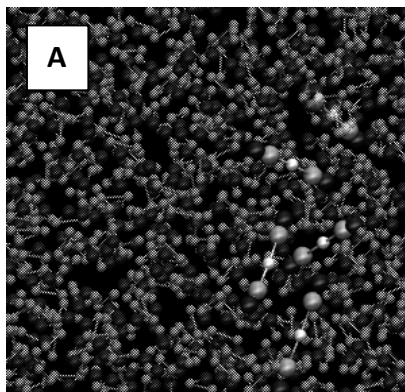






**Figure 5.** Snapshots from MDS of (A)  $\text{Cu}(\text{CN})_2^-$ , (B)  $\text{Au}(\text{CN})_2^-$ , and (C)  $\text{Ag}(\text{CN})_2^-$ . Color codes for (A) blue-nitrogen, cyan-carbon, yellow-metal molecule (Cu), white-counter ion ( $\text{K}^+$ ). (B): blue-nitrogen, cyan-carbon, green-metal molecule (Au), white-counter ion ( $\text{K}^+$ ). Color codes for (C): blue-nitrogen, cyan-carbon, green-metal molecule (Ag), white-counter ion ( $\text{K}^+$ ). (Color image can be viewed from the online version.)





**Figure 6.** Snapshots from MDS of (A)  $\text{Hg}(\text{CN})_2^0$ . Color codes for (A): blue-nitrogen, light blue-cyan-carbon, white-metal molecule (Hg). (Color image can be viewed from the online version.)

