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Mechanism of Zinc Complexation by Alkaline Ligands: A Molecular Modelling Study

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Abstract

In this work, the mechanism of zinc hydroxide and ammine complexation in caustic and ammonia leaching is investigated by molecular modelling using the density functional theory method. The speciation of zinc complexes is defined based on the thermodynamic data and Pourbiax diagrams. The mechanism of Zn+2 complexation by hydroxide and ammine ligands is simulated by molecular modeling. The structure of reactants in the form of individual clusters is modelled using the density function theory. In order to compare the hydroxide and ammine species structures, the geometry studies are carried out as well. The ammoniacal salt effectiveness to improve the dissolution and stability of the ammine species is studied. The ligand single molecule interaction with a smithsonite molecule is done for a better understanding. Molecular modeling show that the zinc hydroxide species are more stable based on the higher reaction free energies. The reaction free energies decrease by adding the OH- and NH3 ions to the complexes from -30.12 kcal/mol to -16.943 kcal/mol, and -22.590 kcal/mol to 66.516 kcal/mol, respectively. The Zn-OH bonds are shorter than Zn-NH3, and the ammine species show more regular structures in comparison with the hydroxide structures. The change of free energies in the presence of ammoniacal salts indicate that the sulfate ions can significantly improve the dissolution of zinc oxide in ammonia. The smithsonite interaction with ammonia and hydroxide reveal that hydroxide ions lead to a higher interaction energy than ammonia (-36.396 vs. -28.238), which is consistent with the higher stability of hydroxide species. The results obtained well-explain the experimental results obtained before, and can be effectively used to optimize the alkaline leaching of zinc oxide ore.

1. Introduction

Zinc oxide minerals such as hemimorphite and smithsonite are alternative sources for zinc production, as high-grade sulfide deposits have been depleted significantly in the last few decades [1, 2]. Hydrometallurgy is the most common method for extraction of zinc from oxide ores [3].

Several leaching agents have been used for dissolution of zinc in oxide ores including inorganic acids as the most common reagent [2, 4, 5] and organic acids [6-8]. Furthermore, the alkaline treatment of low-grade zinc oxide ores has received a lot of attention in the recent years [9-13].

Alkaline leaching mostly by ammonia and soda has a lot of benefits in the hydrometallurgical extraction of zinc [14-17]. The impurities such as Fe, Cu, Cd, Co, and Ni are not leached out in alkaline media, which result in lower reagent consumption. Also zinc solution purification is the most challenging step to produce zinc through hydrometallurgical processes. In alkaline leaching, a higher grade zinc cathode is produced with a lower electricity consumption in the electro-winning process [10]. Another advantage of alkaline leaching is the prevention of passivation layer formation on the particles surface in the presence of carbonate gangue, especially in low-grade zinc oxide ores [1, 18-21]. Also silica gel

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does not form, which is difficult to filtrate and traps zinc in its structure [1, 22].

Dissolution kinetics of alkaline leaching of zinc oxide ores has been studied in recent years for different types of ores. Shrinking core model has been applied for kinetic studies. The alkaline leaching of zinc oxide ores appears both chemically and diffusion control [23-25]. Moreover, the effect of mechanical activation and chelating agents on zinc higher extraction have been investigated [21, 24].

The alkaline dissolution of zinc oxide minerals including smithsonite and hemimorphite is generally described by the following chemical reactions [9, 21]:

$$Zn_4Si_2O_7(OH)_2.H_2O_{(s)} + 12NaOH_{(aq)} \rightarrow 4Na_2Zn(OH)_{4(aq)} + 2Na_2SiO_3 \quad (1)$$

$$Zn_4Si_2O_7(OH)_2.H_2O_{(s)} + 16NH_3 + 2H_2O \rightarrow 4[Zn(NH_3)_4]^{2+} + 8OH^- + 2SiO_2 \quad (2)$$

$$ZnCO_3 + 4NaOH \rightarrow Na_2[Zn(OH)_4] + Na_2CO_3 \quad (3)$$

$$ZnCO_3 + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+} + CO_3^{-2} \quad (4)$$

Based on the Pourbiax diagram for both zinc ammine and hydroxide, several complexes are stable in varying Eh and pH conditions. For Zn hydroxide, seven $Zn(OH)_2$, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, $Zn(OH)_6^{2-}$, Zn_2OH^{3+}, $Zn_4(OH)_4^{4+}$, and $ZnOH^+$, and for ammine, four $Zn(NH_3)_2^{2+}$, $Zn(NH_3)_3^{2+}$, $Zn(NH_3)_4^{2+}$, $ZnNH_3^+$ have been identified. Although alkaline leaching of zinc oxide ores has been the subject of many experimental studies, there are very limited information on the leaching mechanism as well as zinc hydroxide and zinc ammine complexation. Few studies have been performed to understand the mechanism of zinc mineral dissolution in alkaline media based on the leaching residue analysis [23, 26]. However, the spectroscopic studies are subject to many challenges in these meta stable systems as detailed in these investigations. Also the structure of the alkaline complexes is not known, and the factors that affect the stability of these complexes are not researched in details.

Thus the aim of this work is the fundamental study of the mechanism of zinc ammine and hydroxide complexation for the first time to understand species formation in more details. The obtained results can be efficiently used to interpret the results of the previous experimental studies of zinc oxide minerals leaching in alkaline media.

2. Methods

First of all, for molecular modelling of the species, the zinc hydroxide and ammine species were simulated using the Spana software (free version, 2015). The Eh-pH diagrams were produced for the predominant species complexation. Tables 1 and 2 show the reactions based on the Spana simulations for sodium hydroxide and ammonia leaching, respectively. For simplification and minimization of the calculation cost, the complexation of Zn^{+2} was considered in all models, and the results were obtained without the consideration of intermediate products. Zinc oxide minerals like hemimorphite and willemite had siliceous in their structure; however, siliceous precipitates were shown at rarely high alkalinity as amorphous silica.

Table 1. Zinc hydroxide complexes with stability constants (Spana software).

Eq.	Reactions	LogK
5	$Zn^{2+} \rightarrow H^+ + ZnOH^+$	-8.96
6	$Zn^{2+} \rightarrow 2H^+ + Zn(OH)_2$	-16.9
7	$Zn^{2+} \rightarrow 3H^+ + Zn(OH)_3^-$	-28.4
8	$Zn^{2+} \rightarrow 4H^+ + Zn(OH)_4^{2-}$	-41.2
9	$2Zn^{2+} \rightarrow H^+ + Zn_2OH^{3+}$	-9.0
10	$4Zn^{2+} \rightarrow 4H^+ + Zn_4(OH)_4^{4+}$	-27.0
11	$2Zn^{2+} \rightarrow 6H^+ + Zn_2(OH)_6^{2-}$	-54.3

Table 2. Zinc amine complexes with stability constants (Spana software).

Eq.	reaction	LogK
12	$Zn^{2+} + NH_3 \rightarrow ZnNH_3^{2+}$	2.21
13	$Zn^{2+} + 2NH_3 \rightarrow Zn(NH_3)_2^{2+}$	4.5
14	$Zn^{2+} + 3NH_3 \rightarrow Zn(NH_3)_3^{2+}$	6.86
15	$Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+}$	8.89

As Tables 1 and 2 show, by adding more hydroxide and ammonia to the complex structures, the zinc hydroxide and zinc ammonia species became more stable based on LogK.

The reaction mechanism of ammine and hydroxide ions was studied by the molecular modeling simulations. DFT calculations were carried out using the Dmol^3 module implemented in Accelerys Materials Studio, version 2017. The zinc, ammine, and hydroxide ions as well as the produced complexes were modelled using the generalized gradient functional BYLP (exchange functional Becke combined with the Lee–Yang–Parr nonlocal correlation functional) using an Octa-core desktop PC. A double numerical basis set was applied including two atomic orbitals for each occupied orbital for all atoms plus a p-function polarization on hydrogen atoms (DNP) in order to represent hydrogen bonding [27]. The convergence criteria for geometry optimizations are summarized in Table 3.

Table 3. Convergence tolerances for geometry optimization calculations.

Convergence tolerance parameters	Tolerances
Maximum displacement	5×10^{-4} Å
Maximum force	2×10^{-4} Hartrees/Å
Energy	1×10^{-6} Hartrees
SCF	10^{-7} Hartrees
Smearing	No
Orbital cut-off	5.0 Å

No pseudo-potentials or effective core potentials were utilized in this work, and all the results were based on ‘‘all electron relativistic” calculations. In order to represent the local environment, calculations were performed using the continuum solvation model, namely COSMO (COnductor like Screening MOdel) [28]. The dielectric constant of water (78.54) was used to outline the solutions in COSMO, presuming a very dilute medium with minor dielectric constant deviation from pure water. Multipolar expansion was used for calculation of the solvation energy for all the models. The geometry optimization was validated based on the vibrational frequency analysis. The geometry structures were considered optimized where there were no negative frequencies.

In order to investigate the feasibility of the reactions, the interaction energy of the reactions was calculated by molecular modeling. For this purpose, the energy difference of each reaction product was calculated from the energy of the reactants. Although the research work indicates that there is a systematic discrepancy between the free energy computed in molecular modeling by this method and the free energy obtained from thermodynamic measurements [29, 30], it can still serve as a valid basis for comparing the feasibility of different reactions to be used:

$$\Delta G = E_{product} - E_{reactant} \quad (16)$$

where $E_{products}$ is the total energies of the product clusters, and $E_{reactants}$ is the total energy of the reactants. The higher negative amounts of ΔG indicate favorable and stronger reaction compared to the positive or lower negative values [31].

3. Results and Discussion

3.1. Zinc leaching mechanism by NaOH

Figure 1 shows the Pourbiax diagram of zinc hydroxide complexes in different Zn concentrations. Based on the Spana thermodynamic simulations, the most stable form of zinc hydroxide in soda leaching in high concentration of NaOH is Zincate ($Zn(OH)_4^{2-}$). Zincate undergoes Reactions 18-20 by losing OH-groups at a lower pH:

$$NaOH \leftrightarrow Na^+ + OH^- \quad (17)$$

$$Zn^{2+} + OH^- \leftrightarrow ZnOH^+ \quad (18)$$

$$ZnOH^+ + OH^- \leftrightarrow Zn(OH)_2 \quad (19)$$

$$Zn(OH)_2 + OH^- \leftrightarrow Zn(OH)_3^- \quad (20)$$

$$Zn(OH)_3^- + OH^- \leftrightarrow Zn(OH)_4^{2-} \quad (21)$$

Moreover, the Spana simulations showed that zinc concentration was effective on the other complexes of zinc hydroxide formation and their stability such as $Zn(OH)_3^-$. As it is evident from Figure 1, by decreasing the zinc concentration, just zincate appears as a hydroxide complex in the Eh-pH diagrams. These results indicate that zinc could be dissolved by NaOH at potential ranges -1 to 1 V (versus SHE) and at a high pH (above 13).

The zinc hydroxide species were modeled in a molecular scale. Figure 2 shows the zinc hydroxide optimized geometries, and Table 4 presents the free energies of zinc hydroxide complexation resulting from the molecular modeling calculations.

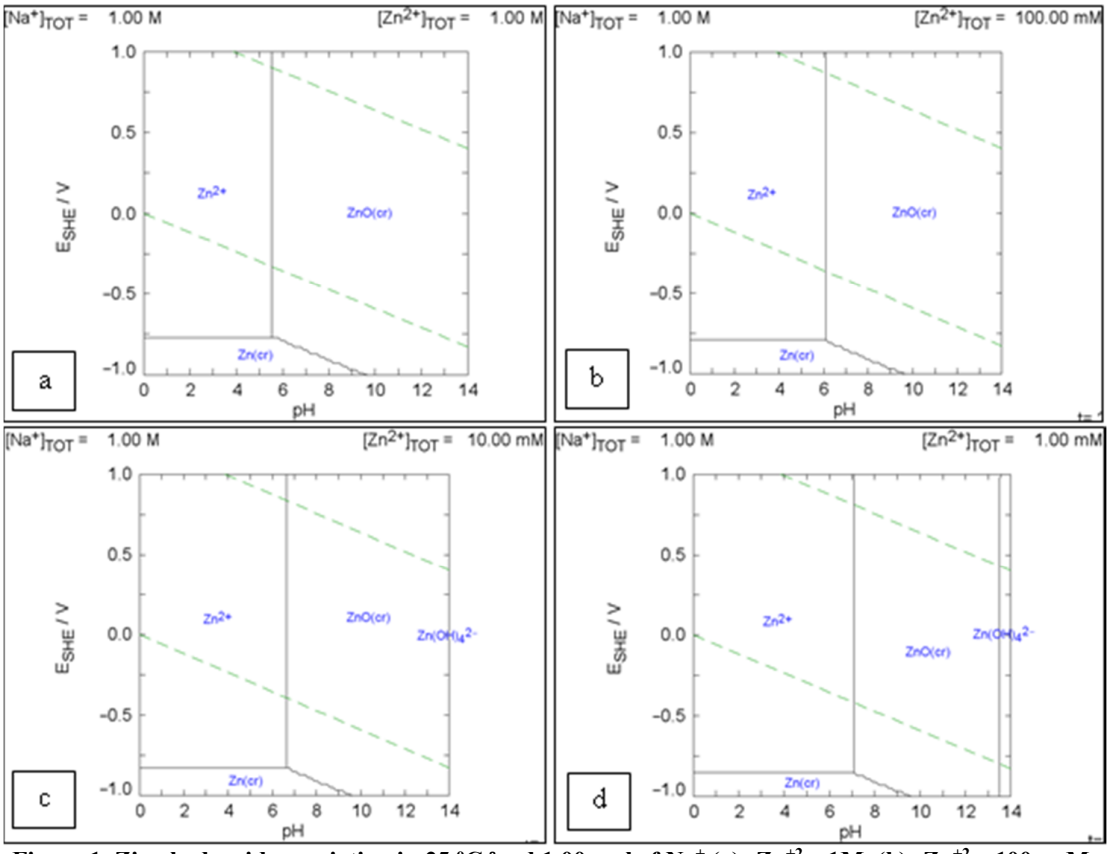


Figure 1. Zinc hydroxide speciation in 25 °C and 1.00 mol of Na^+ (a): Zn^{+2} = 1M, (b): Zn^{+2} = 100, mM, (c): Zn^{+2} = 10 Mm, and (d): Zn^{+2} = 1 Mm.

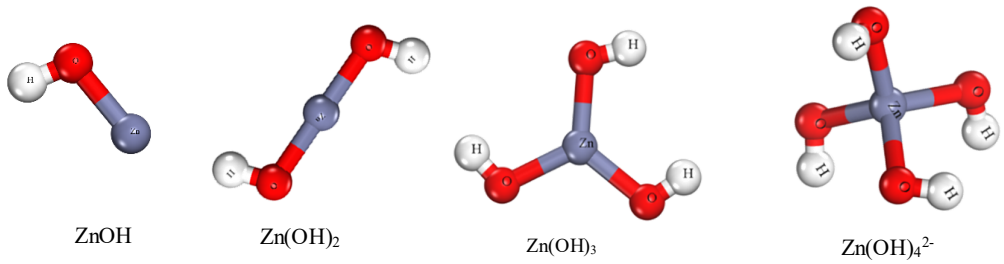


Figure 2. Optimized geometry of zinc hydroxide species.

The geometrical properties of zinc species from the chemistry viewpoint is really important. The chemical bond lengths between the H and O atoms in hydroxide ions were also investigated. The O-H distances from ZnOH to $Zn(OH)_4^-$ were 0.985, 0.980, 0.974, and 0.979 Å, respectively. The results obtained indicate that the chemical bond length from ZnOH to $Zn(OH)_3^-$ decreases, and there is a

little increase in more stable specie of $Zn(OH)_4^{2-}$. Zinc and hydroxide ion bond lengths (ZnOH) in all molecular models increase by adding OH^- ions up to zincate. The measured average bond lengths based on Figure 1 models are 1.815, 1.827, 1.927, and 2.026 Å for ZnOH, $Zn(OH)_2$, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, respectively. It is clear that the bond length enhances slightly as ligand ion (OH^-) bonds increase. None of the models show a linear structure. In all models, zinc and oxygen have a single bond. There is a decreasing trend in the Zn-O-H bond angles except in ZnOH. The average Zn-O-H bond angles are 106.70, 108.15, 107.67, 103.30 degrees for ZnOH, $Zn(OH)_2$, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$, respectively. $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ have trigonal and tetrahedral structures.

The O-Zn-O angles were measured after geometry optimization. The obtained values indicate no equal angles in each model. The average angles are 180, 178.70, 120, and 107.80 degrees for ZnOH, $Zn(OH)_2$, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$, respectively.

As Table 4 displays, the reaction free energies decrease by adding OH^- ions to the complexes. The reaction total free energy for reactions 4 and 1 were the lowest and the highest, respectively. The zincate speciation total free energy is -16.943 kcal/mol. The Spana simulations were validated by molecular modeling results with the decreasing trend in the reaction free energies. As shown in Table 4, the total reaction energies of Zn and OH^- are far more than zero, and prove that zinc hydroxide complexation occurs readily. A more negative reaction energy indicates that the reaction occurs more easily.

Table 4. Zinc hydroxide reaction energies in (kcal/mol).

Reaction	ΔG (kcal/mol)
$Zn^{2+} + OH^- \leftrightarrow ZnOH^+$	-30.12
$ZnOH^+ + OH^- \leftrightarrow Zn(OH)_2$	-35.141
$Zn(OH)_2 + OH^- \leftrightarrow Zn(OH)_3^-$	-21.336
$Zn(OH)_3^- + OH^- \leftrightarrow Zn(OH)_4^{2-}$	-16.943

3.2. Zinc leaching mechanism by ammonia

The leaching mechanism of zinc oxide minerals with ammonia or ammonium salts is presented in this section. Figure 3 shows the Spana simulations of zinc ammine speciation in different Zn^{+2} concentrations. Based on the Spana simulations, the most stable zinc ammine species is $Zn(NH_3)_4^{2+}$. Reactions 22-27 show the proposed mechanism of $Zn(NH_3)_4^{2+}$ formation:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (22)$$

$$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+ \quad (23)$$

$$Zn^{2+} + NH_3 \leftrightarrow ZnNH_3^{2+} \quad (24)$$

$$NH_3 + ZnNH_3^{2+} \leftrightarrow Zn(NH_3)_2^{2+} \quad (25$$

$$NH_3 + Zn(NH_3)_2^{2+} \leftrightarrow Zn(NH_3)_3^{2+} \quad (26)$$

$$NH_3 + Zn(NH_3)_3^{2+} \leftrightarrow Zn(NH_3)_4^{2+} \quad (27)$$

As Figure 3 shows in alkaline solution of ammonia and in all zinc cencentrations and ammonia constant concentration, $ZnNO_3^+$ and $ZnNO_2^+$ can be formed at rarely simailr thermodynamical conditions. It is clear that under certain conditions and decrease in zinc concentration but keeping the other conditions constant results in formation of $Zn(NO_2)_2$, specially in an acidic pH. Beside, the stability regions of $Zn(NH_3)_4^{2+}$ and $Zn(OH)_4^{2-}$ increases by reduction of zinc concentration. Note that at a lower zinc concentration (b, c, d), $Zn(NH_3)_4^{2+}$ stability ranges are at pH = 8.5-10 and Eh = -1-0 but at a lower zinc concentration, $Zn(NH_3)_4^{2+}$ forms at a slightly lower pH = 7-10 and Eh = -1–0. Above pH 12, ammonia has no ability for compexation, and crystalline ZnO is stable. Obviously, at higher Eh ranges, the zinc ammine species are not stable. Based on these results, a higher concentration of ammonia is required to form stable $Zn(NH_3)_4^{2+}$.

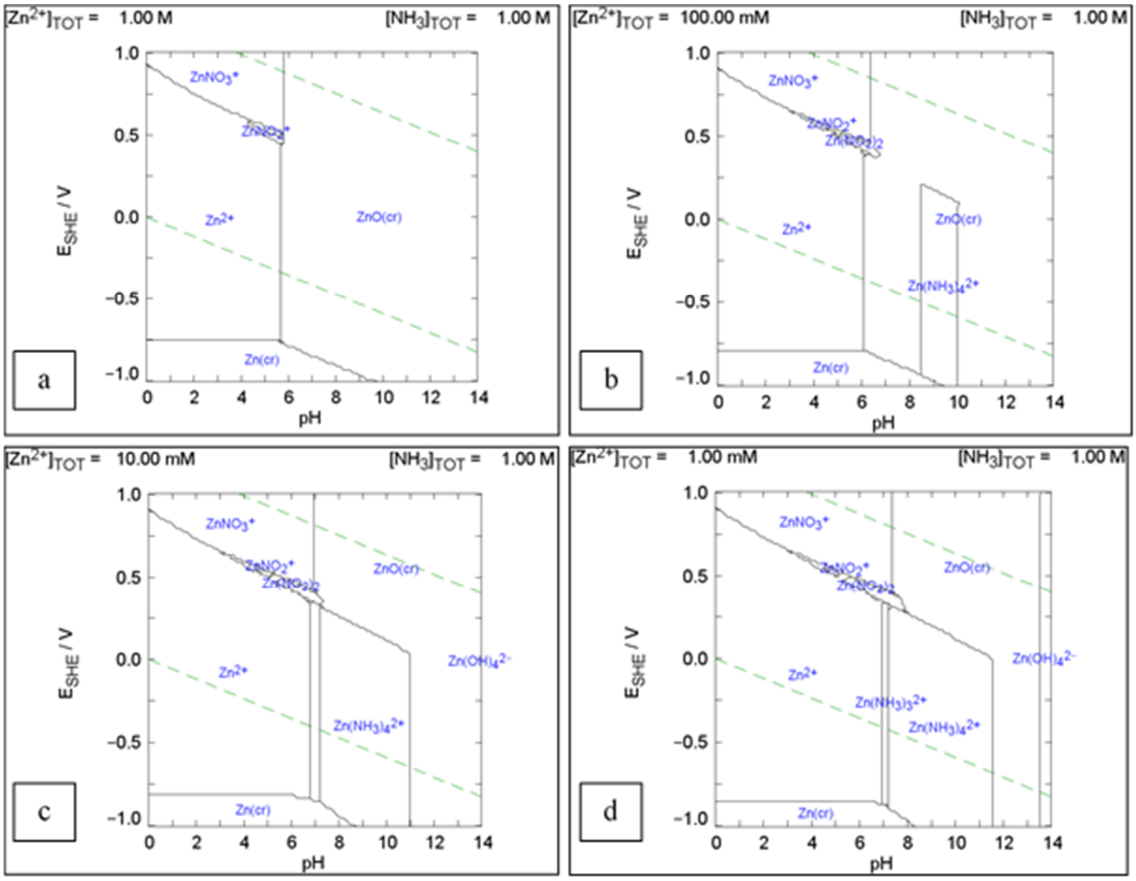
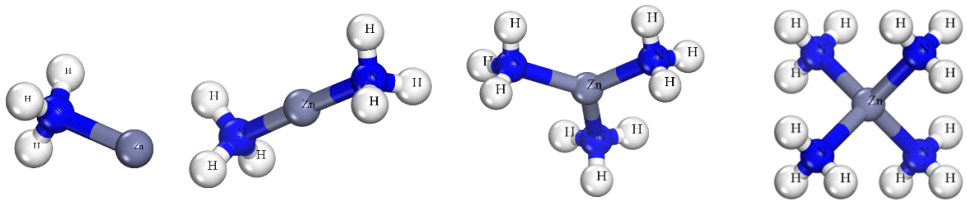


Figure 3. Zinc ammine speciation in 25 ºC ˚and 1.00 mol of Na^+ (a) Zn^{+2} = 1 M, (b): Zn^{+2} = 100 mM, (c): Zn^{+2} = 10 Mm, and (d): Zn^{+2} = 1 Mm.

Figure 4 shows the optimized geometries of zinc ammine molecular models. The zinc and nitrogen bond lengths show that by ammonia adding, the length of the chemical bond increases. The Zn-N average bond lengths are 1.934, 1.925, 2.014, and 2.708 Å for $Zn(NH_3)^{2+}$, $Zn(NH_3)_2^{2+}$,$Zn(NH_3)_3^{2+}$, and $Zn(NH_3)_4^{2+}$, respectively. The N-Zn-N bond is linear (180 degrees) in model $Zn(NH_3)_2^{2+}$ but non-linear in $Zn(NH_3)_3^{2+}$ and $Zn(NH_3)_4^{2+}$, making trigonal and tetragonal geometrical zinc ammine species. The model $Zn(NH_3)_2^{2+}$ is rarely linear, and the average bond angles are 177.31, 120, and 109.471 degrees for $Zn(NH_3)_2^{2+}$, $Zn(NH_3)_3^{2+}$, and $Zn(NH_3)_4^{2+}$, respectively.

The effect of complex orders on the NH_3 bond lengths (N-H) and bond angles (H-N-H) was investigated. In comparison between the highest order complex of zinc ammine $Zn(NH_3)_4^{2+}$ and free ammonia NH_3, the bond lengths are both 1.025 Å, similarly. There is no significant change in the first, second, and third order bond lengths as 1.03, 1.0325, and 1.0285, respectively.

Free ammonia has the lowest H-N-H bond angles (104.543 degrees) and the highest one is first order complex $Zn(NH_3)^{2+}$ (109.384 degrees). The second, third, and fourth orders have similar bond angles but the third and fourth orders are very close as 107.655, 106.897, and 106.405 degrees, respectively. It is clear that the number of ligands (NH_3) have no significant effect on each other properties. Among all the ammine species, $Zn(NH_3)_4^{2+}$ has more uniform geometric structure because of the same lengths of the bonds and similar bond angles.



$Zn(NH_3)^{2+}$ $Zn(NH_3)_2^{2+}$ $Zn(NH_3)_3^{2+}$ $Zn(NH_3)_4^{2+}$

Figure 4. Optimized geometry of zinc ammine species.

Table 5 shows the zinc and ammonia reaction free energies. As it is shown, $Zn(NH_3)_4^{2+}$ has the lowest free energy in comparison with the other zinc ammine spiecies. The zinc ammine species complexation total energy increases from $ZnNH_3^{2+}$ to $Zn(NH_3)_4^{2+}$. The lowest total energy of zinc ammine complextation belongs to $ZnNH_3^{2+}$. The values obtained in this work show a sharp increase in the total energies by adding more NH_3 to the zinc ammine species.

Ligand addition to the structures have large effect on the reactants and reaction total free energies. As it is shown (Table 5) and based on the decreasing free energies of products, it can be concluded that the ligand high concentration is a very important factor, and favours formation of more stable complexes.

Table 5. Zinc ammine reaction energies in (kcal/mol).

Reaction	ΔG (kcal/mol)
$Zn^{2+} + NH_3 \leftrightarrow ZnNH_3^{2+}$	-22.59
$NH_3 + ZnNH_3^{2+} \leftrightarrow Zn(NH_3)_2^{2+}$	-25.1
$NH_3 + Zn(NH_3)_2^{2+} \leftrightarrow Zn(NH_3)_3^{2+}$	-16.942
$H_3 + Zn(NH_3)_3^{2+} \leftrightarrow Zn(NH_3)_4^{2+}$	66.516

As the leaching process by alkaline reagents has a lower extraction than acidic leaching, in order to improve zinc dissolution, alternative ways like mechanical activation and adding ammonia salts were used. In this section, the effect of the presence of ammonia salts in addition to ammonia that release anoins in solution was investigated. The results obtained reveal the role of ammonia salts in leaching improvement.

Free energies of interaction of zinc, ammonia, and CO_3^{2-}, SO_4^{2-}, and Cl^- anoins were calculated by molecular modeling. Figure 5 shows the optimized geomtry structure of interacted zinc, ammonia, and anions. Changes in the interation free energies completely reflect the effects of ammonia salts. The optimised geometries clearly show the tendency of nitrogen atom of ammonia to orrient with the zinc atoms in the presence of other intermediates.

As Figure 5 shows, ammonia interaction with zinc in the presence of sulfate ion shifts toward a more negative value of interaction free energy compared with just ammonia and zinc. In other words, ammonium sulfate is more effective for zinc dissolution with ammonia, and leads to the formation of stronger species. This outcome signifies that in the presense of sulphate anoin, adsorption of ligand on the zinc minerals surface occures readily, and it reinforces the leaching process. Moreover, this finding confirmed the prevoius study results that ammonia salts improved the ammonia leaching process, and zinc dissolution increases. Based on Figure 5, free energies of species are in the following order:

$$Zn + NH_3 + SO_4^{2-} > Zn + NH_3 + Cl^- > Zn + NH_3 + CO_3^{2-} > Zn + NH_3$$

Thus the reactivity of ammonia with zinc has a lower interaction energy than $Zn + NH_3 + SO_4^{2-}$. Consequently, these results indicate that addition of ammonia salts favors the alkaline leaching of zinc oxides.

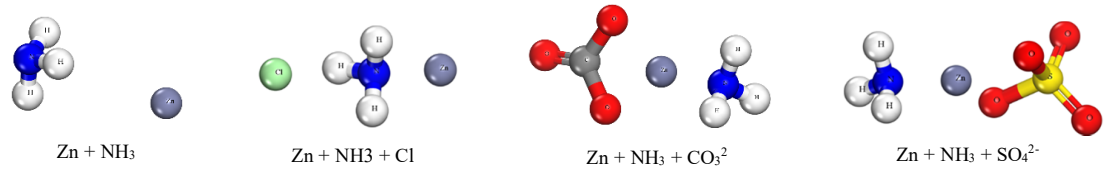


Figure 5. Interaction of ammonia salt anoins with zinc.

In order to get more insight toward the interaction properties of zinc oxide minerals and alkaline agents, smithsonite mineral in the form of single cluster was investigated (Figure 6). Similar to the prevoius sections, Figure 6 demonstrates that the N and O atoms orient toward zinc atom in the smithsonite molecule. Table 6 indicates that OH^- ligand has a stronger interaction than NH_3. The first reaction shows -28.238 Kcal/mol interacton energy, similar to the Table 5 data. On the other hand, hydroxide ligand interaction energy is in good agreement with the Table 4 data.

The Zn-O and Zn-N distances are 1.848 and 1.977 angstrom, respectively. This coubld be attributed to the higher ability of hydroxide for complexation with zinc than ammonia.

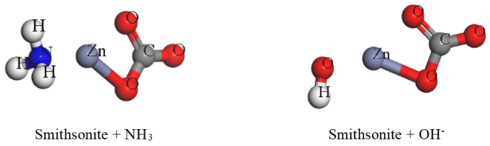


Figure 6. Alkaline ligands interaction with Zn^{+2}.

Table 6. Smithsonite single cluster interaction with hydroxide and ammonia.

Interacting species	Interaction energy (kcal/mol)
Smitsonite + NH_3	-28.238
Smitsonite + OH^-	-36.396

4. Conclusions

Accourding to the results obtained, it can be concluded that a higher concentration of alkaline ligands is required for zinc dissolution. In ammoniacal leaching, at lower pH and Eh, zinc dissolution and stable forms occur.

Molecular modeling showed that the zinc hydroxide species were more stable based on the higher reaction free energies. The reaction free energies indicate a downward trend in the complexation of zinc species to reach more stable species. $Zn(NH3)_4^{2+}$ has the most regular structure among the other structures. The Zn-OH bonds are shorter than Zn-NH_3, and ammine species show a more regular staructure in camparison to the hydroxide strucrure, generally.

The change of free energies in the presence of ammoniacal salts indicate that sulfate ion (ammonium sulfate) is more effective in the stability. Thus the combination of ammonium sulfate and ammonia could result in improved dissolution, and a more stable species formation.

The smithsonite interaction with ammonia and hydroxide revealed that hydroxide led to a higher interaction energy than ammonia. This result is consistent with the higher stability of hydroxide species. The results obtained revealed that Zn^{+2} reaction energy correlated well with the interaction energy of smithsonite single cluster model.

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مکانیزم تشکیل کمپلکس روی به وسیله لیگاندهای قلیایی: مطالعه مدلسازی مولکولی

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چکیده:

در این تحقیق، مکانیزم کمپلکس‌سازی هیدروکسید و آمونیوم روی در لیچینگ قلیایی و آمونیاکی به روش مدل‌سازی مولکولی و با روش تئوری تابع چگالی بررسی شده است. گونه‌شناسی کمپلکس‌های روی بر اساس داده‌های ترمودینامیکی و نمودارهای پوربه تعیین شد. ساختار واکنش‌دهنده‌ها به شکل کلاسترهای جداگانه با روش تئوری تابع چگالی مدل‌سازی شد. برای مقایسه ساختار گونه‌های هیدروکسید و آمین، مطالعات ساختاری نیز انجام شد. اثر نمک آمونیاک در بهبود و پایدارسازی گونه‌های آمین مطالعه گردید. برای فهم بهتر، اندرکنش تک‌مولکول‌های لیگاند با مولکول اسمیت‌زونیت نیز انجام شد. نتایج مدل‌سازی مولکولی نشان داد که گونه‌های هیدروکسیدی روی به‌دلیل انرژی آزاد منفی بالاتر پایدارتر هستند. انرژی واکنش با افزایش تعداد یون‌های OH^- و NH_3 در کمپلکس‌ها به ترتیب از ۳۰/۱۲- به ۱۶/۹۴۳- کیلوکالری بر مول و از ۲۲/۵۹۰- به ۶۶/۵۱۶- کیلوکالری بر مول کاهش یافت. پیوندهای Zn-OH کوتاهتر از $Zn-NH_3$ بوده و گونه‌های آمین ساختار منظم‌تری در مقایسه با ساختارهای هیدروکسیدی دارند. تغییر انرژی آزاد در حضور نمک‌های آمونیاکی معرف آن است که یونهای سولفات می‌توانند به‌طور قابل‌ملاحظه‌ای انحلال اکسید روی در آمونیاک را بهبود دهند. اندرکنش اسمیت‌زونیت با آمونیاک و هیدروکسید نشان می‌دهد یون‌های هیدروکسیدی منجر به انرژی اندرکنش بالاتری نسبت به آمونیاک (۳۶/۳۹۶- در مقابل ۲۸/۲۳۸-) شده که با پایداری بالاتر گونه‌های هیدروکسیدی مطابقت دارد. نتایج به دست آمده به‌خوبی نتایج آزمایشگاهی به دست آمده قبلی را توضیح داده و به‌طور مؤثری می‌تواند در بهینه‌سازی لیچینگ قلیایی کانسنگ‌های اکسیدی روی مورد استفاده قرار گیرد.

کلمات کلیدی: اکسید روی؛ لیچینگ قلیایی؛ مدل‌سازی مولکولی؛ اسمیت‌زونیت؛ آمونیاک