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Molecular Dynamics Study on the Leaching of Zinc-Bearing Dust Sludge by Choline Chloride-Malonic Acid

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Abstract: Molecular dynamics of the interaction between four metal oxides (ZnO, Fe₂O₃, Al₂O₃, and CaO) present in zinc-bearing dust sludge and choline chloride (ChCl)-malonic acid (MA)(1:2) was studied in this work using Materials Studio software. The interaction mechanism was revealed by analyzing the interaction energy and radial distribution function from the perspective of quantum mechanics, and the simulation results were verified by single factor leaching experiments. The calculation results show that the complete cleavage surface of the four metal oxides is the (001) surface, and ChCl-2MA forms a stable structure with multiple intermolecular hydrogen bonds centered on the chlorine atom. The dynamic simulation of the interaction model shows that strength of interaction between ChCl-2MA and the four metal oxides follows the order: ZnO > Fe₂O₃ > Al₂O₃ > CaO. ChCl-2MA mainly interacts with ZnO by chemical adsorption, while ChCl-2MA mainly interacts with Fe₂O₃, Al₂O₃, and CaO by physical adsorption. The radial distribution function shows that Cl in ChCl-2MA and C=O in MA form chemical bonds with Zn in ZnO, and the choline cation (Ch⁺) forms C-H···O with ZnO. Among these bonds, the Cl-Zn bond energy is stronger. During the interaction between ChCl-2MA and Fe₂O₃ and Al₂O₃, O-H···O and C-H···O are formed and interact with CaO by van der Waals force. Single factor leaching experiments show that, under the same leaching conditions, the leaching rate of ZnO by ChCl-2MA is greater than 90%, while the leaching rate of Fe₂O₃, Al₂O₃, and CaO is about 10%. These results indicate good selectivity of ChCl-2MA for ZnO in the zinc-bearing dust sludge. The above conclusions have important theoretical significance and provide an in-depth understanding of the leaching mechanisms of zinc-bearing dust sludge in deep eutectic solvents.

Keywords: zinc-bearing dust sludge; choline chloride-malonic acid; molecular dynamics; interaction energy; radial distribution; selective leaching

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1. Introduction

Zinc is an important strategic base material, which is often used in alloy production, medical industry, chemical industry, high-tech applications, and certain other fields. Due to the growing demand for zinc resources, high-grade, easily mineable, and easy flotation-containing zinc mineral resources are depleting. As a result, there is an imbalance between the demand and supply of zinc metal that causes serious obstacles to social progress [1]. Meanwhile, with the rapid economic development and social progress, the demand for crude steel has increased significantly, and a large amount of zinc-bearing dust sludge is produced in the production of crude steel [2]. Zinc-bearing dust sludge is a complex solid waste, which mainly consists of metal oxides, such as Fe₂O₃, ZnO, Al₂O₃, CaO, MgO, Fe₃O₄, and CaCO₃ [3]. In terms of the content, the production of zinc-bearing dust sludge is only about 10–12% of the total output of crude steel. However, the accumulation of excessive raw materials caused by insufficient recovery and utilization of zinc-bearing dust

sludge has caused serious concerns about the health of ecosystems and humans [4,5]. At present, zinc recovery from zinc-bearing dust sludge is becoming an important pathway to obtain zinc resources [6]. However, there are some drawbacks in the traditional treatment of zinc-bearing dust sludge. For example, the acid leaching treatment in the wet treatment process consumes a large amount of acid. Moreover, iron can easily enter the leaching solution and lead to further complexities to remove iron from the leaching solution [7,8]. The ammonia leaching process has the problem of poor dissolution of zinc ferrite, which results in various challenges such as low leaching rate and high ammonia volatility [9,10]. In recent years, deep eutectic solvents have been introduced as novel solvents in the field of wet zinc extraction technology. These solvents can be used to leach zinc-bearing dust sludge and are gradually replacing the traditional acid leaching and ammonia leaching processes.

Deep eutectic solvents (DESs) are eutectic mixtures composed of hydrogen-bond donors and hydrogen-bond acceptors, which result in a liquid at room temperature when mixed in a certain molar ratio [11]. As novel green solvents, DESs have attracted extensive attention from researchers all over the world due to various advantages, such as biodegradability, low price, 100% atom utilization during the synthesis process, and good application prospects in many fields including separation processes and chemical reactions [12,13]. Lei [14] used choline chloride-urea (ChCl-urea) as deep eutectic solvent and added 0.1 mol/L ammonia triacetic acid to leach up to 87% of zinc in the zinc-bearing dust sludge. Zhang [15] studied the leaching of ZnO using ChCl and oxalic acid and found that more than 90% ZnO could be leached at a liquid-to-solid ratio of 10:1, leaching temperature of 50 °C, leaching time of 2 h, and a mixing speed of 300 r/min. Ashraf [16] dissolved the zinc-bearing dust sludge in a deep eutectic solvent of ChCl-urea and extracted a product containing 38% zinc from the dust under certain conditions. Zhu [17] used ChCl-urea-ethylene glycol to recover zinc from ZnO dust and found that the leaching rate of zinc was about 85.2% when the pulp concentration, temperature, and stirring speed were 50 g/L, 80 °C, and 600 r/min, respectively.

Although choline-based deep eutectic solvents have demonstrated good progress in the leaching of zinc-bearing dust sludge, the molecular analysis of the interaction mechanism between the four metal oxides and a 1:2-mixture of choline chloride and malonic acid (ChCl-2MA) has not yet been reported. In this study, the quantum mechanics software Materials Studio[®] was used to simulate the crystal structure of the metal oxides and the stable configuration of the deep eutectic solvent. Moreover, an interaction model between the deep eutectic solvent and the complete dissociation surface of metal oxides was also proposed. The proposed interaction model of the deep eutectic solvent and the metal oxides was based on molecular dynamics, and the interaction energy and radial distribution were calculated to analyze the interaction mechanism between four metal oxides and ChCl-2MA. The accuracy of the molecular simulation results was verified using single factor leaching experiments.

2. Modeling and Calculations

2.1. Composition Analysis of Zinc-Bearing Dust Sludge

The zinc-bearing dust sludge was taken from a steel plant in Hebei, China. The main oxide components were analyzed using X-ray fluorescence (XRF, Chuang Xiang Yi Qi, Beijing China), and the corresponding results are presented in Table 1. The results show that the zinc-bearing dust sludge contained 48.20% Fe₂O₃, 25.32% ZnO, 6.20% Al₂O₃, and 3.95% CaO. Moreover, SO₃ was heated to produce SO₂ gas. The oxide content after the conversion of SO₃ to volatile SO₂ decreased, thus reducing its effect on the leaching of ZnO. Therefore, the four metal oxides (ZnO, Fe₂O₃, Al₂O₃, and CaO) and ChCl-2MA were subjected to molecular dynamics simulation, followed by experimental verification of the proposed model.

Table 1. Chemical composition analysis of zinc-bearing dust sludge (content.%).

Element	Fe ₂ O ₃	ZnO	Al ₂ O ₃	CaO	SO ₃	SiO ₂	MgO	PbO	K ₂ O	MnO
Content %	48.20	25.32	6.20	3.95	3.47	2.93	1.95	1.06	0.74	0.26
Standard deviation	0.01	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.03	0.03

2.2. Modeling of Metal Oxide Structures and their Cleavage

2.2.1. Exchange—Correlation Energy Functionals Test

According to Joint Committee on Powder Diffraction Standards (JCPDS), the ZnO lattice parameters are $a=b=3.2498 \text{ \AA}$ and $c=5.2066 \text{ \AA}$. The Fe₂O₃ lattice parameters are $a = b = c = 5.42 \text{ \AA}$ and $\alpha = \beta = \gamma = 55.36^\circ$. The Al₂O₃ lattice parameters are $a = b = 4.759 \text{ \AA}$, $c = 12.991 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$. The lattice parameters of CaO are $a = b = c = 4.811 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. The calculations of the four crystal models were conducted under the Castep module using Materials Studio[®] software (Materials Studio 2019, Accelrys, San Diego, CA, USA) [18,19]. The BFGS optimization algorithm was used in the calculations, and the interaction between the real ion and the valence electron was described by the ultrasoft pseudopotential. The accuracy of the calculations was ‘Fine’. TS method was used for DFT-D correction. LDA+U method was used to modify its electronic properties [20–22]. The orbital valence electrons were as follows: Fe-3d⁶4s², Zn-3d¹⁰4s², Al-3s²3p¹, Ca-4s², and O-2s²2p⁴. The standard parameters of convergence were as follows: the energy convergence value was $1.0 \times 10^{-5} \text{ eV/atom}$; the maximum force between the atoms was $0.05 \text{ eV/\AA}$; the maximum internal stress was 0.1 GPa ; the maximum displacement was $0.002 \text{ \AA}$. By analyzing cell parameters and total energy calculated by different exchange–correlation energy functionals, the optimal exchange energies were obtained, as shown in Table 2. [23]

Table 2. Optimization results of exchange–correlation energy functionals.

Metal Oxide	Exchange–Correlation Energy	Cell Parameters		Error/%		Total Energy/eV
		a	c	a	c	
ZnO	LDA(CA-PZ)	3.191	5.158	1.81	0.93	−4300.24
	GGA(PBE)	3.289	5.309	1.21	1.97	−4294.54
	GGA(RPBE)	3.319	5.358	2.15	2.91	−4296.55
	GGA(PW91)	3.288	5.291	1.18	1.62	−4299.28
	GGA(PBEsol)	3.269	5.225	0.62	0.38	−4299.26
Fe ₂ O ₃	LDA(CA-PZ)		5.319		1.86	−6060.58
	GGA(PBE)		5.342		1.44	−6079.93
	GGA(RPBE)		5.369		0.94	−6089.15
	GGA(PW91)		5.355		1.19	−6090.99
	GGA(PBEsol)		5.286		2.58	−6046.69
Al ₂ O ₃	LDA(CA-PZ)	4.705	12.803	1.13	1.44	−2864.36
	GGA(PBE)	4.787	13.1	0.58	0.83	−2861.77
	GGA(RPBE)	4.682	12.709	0.16	2.17	−2863.81
	GGA(PW91)	4.784	13.083	0.52	0.7	−2865.34
	GGA(PBEsol)	4.783	13.001	0.5	0.07	−2854.57
CaO	LDA(CA-PZ)		4.732		1.64	−1414.49
	GGA(PBE)		4.733		1.62	−1441.65
	GGA(RPBE)		4.353		9.51	−1442.62
	GGA(PW91)		4.745		1.37	−1442.83
	GGA(PBEsol)		4.714		2.05	−1438.57

The results presented in Table 2 show the optimized values of different exchange–correlation energy functionals, which indicate that the total energy of ZnO was always maintained at about −4300 eV under various exchange–correlation energy functionals calculations. The cell parameter error calculated by GGA (PBEsol) exchange–correlation energy functional was the smallest among all exchange–correlation energy functionals, and the lattice constant error was within 2%. At the same time, the calculated cell parameters

of ZnO were in agreement with experimental reports, so GGA (PBEsol) was selected to calculate the ZnO crystal cell [24]. The cell parameter error $a = b = c = 0.941\%$ of Fe_2O_3 obtained under GGA (RPBE) exchange–correlation energy functional was the smallest error among all exchange–correlation energy functionals values, and the total energy of -6089.15 eV was not very different from the optimal parameter. Therefore, GGA (RPBE) was selected to calculate the Fe_2O_3 crystal cell. The simulation results were in good agreement with the experimental results [25]. GGA (PW91) was selected to calculate the Al_2O_3 crystal cell, the results of which were consistent with the experimental results. The parameters of GGA (PBEsol) exchange–correlation energy functional had the smallest error, but the total energy was the largest [26]. The cell parameter error of CaO calculated by GGA (PW91) was the best parameter among all related energy calculations, and the total energy was not different from -1414.49 eV calculated by LDA (CA-PZ). Therefore, GGA (PW91) was selected to calculate the CaO cell. The simulation results were in good agreement with the experimental results [27].

2.2.2. Complete-Cleavage Surface Calculations

During the leaching of zinc-bearing dust sludge, the adsorption of the agent mainly occurs on the mineral surface. In the process of crushing, grinding, and other processing steps, minerals are fractured along the surface with weak bonding inside the crystal under the action of external forces, forming a stable surface with low surface energy. That is, the lowest surface energy is the complete-cleavage surface [28,29]. For this reason, the surface energy of the common surfaces of the four metal oxides was calculated in the current study to determine the complete cleavage. The smaller the surface energy, the easier it is to become the surface of the mineral-drug [30]. The results presented in Table 3 show the common surface energy values of the four metal oxides.

Table 3. Common surface energies of metal oxides (J/m^2).

Metal Oxide	001	011	111	101	110
ZnO	0.8177	3.9275	3.9271	2.0852	2.4053
Fe_2O_3	1.9021	1.9425	1.9326	1.9836	1.9308
Al_2O_3	1.7651	2.1034	-	-	2.1127
CaO	1.1723	1.5974	1.7486	1.7942	1.5813

The surface energy is calculated using Equation (1).

$$E_{\text{surf}} = \frac{E_{\text{slab}} - \left(\frac{N_{\text{slab}}}{N_{\text{bulk}}}\right)E_{\text{bulk}}}{2A} \quad (1)$$

where E_{slab} and E_{bulk} refer to the total energy of the mineral layer crystal model and the unit cell model, respectively (eV), N_{slab} refers to the total number of atoms in the layer crystal model, N_{bulk} is the total number of atoms in the unit cell model, A is the area of the layer crystal model along the Z-axis ($\times 10^{-20} \text{ m}^2$), and '2' accounts for the two surfaces along the Z-axis of the layered crystal model.

The results presented in Table 3 show the surface energy of the common surfaces of the four metal oxides and reveal that the surface energy of ZnO (001) surface $E_{\text{surf}} = 0.8177 \text{ J}/\text{m}^2$ was the smallest among the five surface energies, indicating that the ZnO (001) surface underwent complete cleavage. The surface energy of Fe_2O_3 (001) ($E_{\text{surf}} = 1.9021 \text{ J}/\text{m}^2$) was the lowest among the common surfaces. Therefore, it was inferred that Fe_2O_3 underwent complete cleavage. For the common surfaces of Al_2O_3 (001), the surface energy value ($E_{\text{surf}} = 1.7651 \text{ J}/\text{m}^2$) indicated complete cleavage of Al_2O_3 . The surface energy of CaO (001) surface ($E_{\text{surf}} = 1.1723 \text{ J}/\text{m}^2$) was the lowest among the five surface energies, indicating complete cleavage. The complete-cleavage surfaces of four metal oxides obtained by surface energy calculations were in agreement with the experimental results previously reported, which proves the reliability of the complete-cleavage surfaces obtained by surface energy calculation [31–33].

2.2.3. Density of States Analysis

Calculating the metal oxide cell and the complete-cleavage surface state density can provide the surface atomic activity size because the physical and chemical reactions always occur near the Fermi level. The closer to the Fermi level, the stronger the electronic activity. The farther the energy level, the lower the energy. In the latter case, the electron does not easily participate in the reaction [34–36]. Figure 1 shows the comparison of the density of states of the four single minerals; the dotted green lines indicate the Fermi energy levels of each metal oxide.

By comparing the density of states of ZnO cell and complete-cleavage surface, it is found that the peak of the complete cleavage surface increased at the highest occupied state. Moreover, the peak rose, mainly because the O-2p and Zn-3d contributed to the highest occupied state; the Zn-3d orbital contributed more than the O-2p orbital. The results also show that the surface Zn activity of ZnO (001) was relatively high. By comparing the Fe₂O₃ cell and complete-cleavage surface state density, it can be seen that the highest occupied state of the complete-cleavage surface near the Fermi level shifted to the left, while the highest occupied peak area became larger and the peak value increased. This was mainly due to the increase in the peak areas of Fe-3d and O-2p orbitals near the Fermi level, indicating that both Fe and O activities in the Fe₂O₃ (001) surface increased. By comparing the density of states of the Al₂O₃ cell and the complete-cleavage surface, it is found that the peak of the total density of states of the complete-cleavage surface increased, which is mainly due to the increase in the density of state of O-2p, indicating that O in the Al₂O₃ (001) surface was more active and reacted more easily with foreign substances than other species. By comparing the density of states of the CaO cell and the complete-cleavage surface, it can be seen that the peak density of states of the complete-cleavage surface increased, which is mainly because the peaks of Ca and O partial-wave density of states increased. The peak of the density of states near the Fermi level was mainly contributed by O-2p, indicating that O was more likely to react with foreign substances in the complete-cleavage surface of CaO. In short, considering the complete-cleavage surface of the four metal oxides, Zn was more active than O in the ZnO (001) surface, whereas Fe and O had similar activities in the Fe₂O₃ (001) surface. Moreover, O in Al₂O₃ (001) and CaO (001) was more active than Al and Ca.

2.3. Construction and Calculation of Eutectic Solvent Model

In the current study, ChCl was used as the hydrogen bond acceptor, while MA was used as the hydrogen bond donor. Both ChCl and MA were used in a 1:2 molar ratio to simulate the ChCl-2MA cluster model. Dmol3 module in Materials Studio was used to build the cluster model. A generalized gradient was used in the construction of the model. In addition, approximation (GGA) and BLYP density functional were used, while the calculation accuracy was 'Fine'. The DNP 4.4 basis set was selected, and the total energy convergence value of the system was 1.0×10^{-5} eV/atom. Moreover, the maximum internal stress was 0.002 Ha/Å, and the maximum displacement was 0.005 Å. All-electronic nuclear processing method was selected for the simulation [37]. The phonon spectra of ChCl-2MA and the optimized stable configuration of ChCl-2MA were obtained from the simulation. Figure 2 shows the phonon spectrum of the stable configuration of ChCl-2MA deep eutectic solvent. Furthermore, Figure 3 shows the stable configuration of ChCl-2MA deep eutectic solvent.

Figure 1. Density of states contrast diagram of metal oxides. Comparison of ZnO density of states ((a): ZnO cell (b): ZnO (001) surface). Comparison of Fe₂O₃ density of states ((c): Fe₂O₃ cell (d): Fe₂O₃ (001) surface). Comparison of Al₂O₃ density of states ((e): Al₂O₃ cell (f): Al₂O₃ (001) surface). Comparison of CaO density of states ((g): CaO cell (h): CaO (001) surface).

Figure 2. Phonon spectrum of ChCl-2MA deep eutectic solvent.

Figure 3. Stable configuration of ChCl-2MA deep eutectic solvent.

As can be seen from Figure 2, in the process of forming the stable configuration of ChCl-2MA deep eutectic solvent, the X-coordinate turned out to be negative, while part of the value was uncountable, indicating that the formed ChCl-2MA deep eutectic solvent had a fixed structure without any virtual frequency. As seen from Figure 3, the stable structure formed by ChCl and MA was a multi-molecular hydrogen bond structure

centered on the chlorine atom, which played a crucial role in the stability of intermolecular hydrogen bonds.

3. Calculation and Analysis of the Interaction

3.1. Construction of the Interaction Model

The establishment of a stable interaction model is the premise for analyzing the interaction mechanism by ChCl and MA on the complete-cleavage surface of the four metal oxides and the basis of molecular dynamics simulation. Therefore, by optimizing the surface model of the complete-cleavage surface of the four metal oxides and the stable ChCl-2MA eutectic solvent model, the ‘Build Layer’ was used to add the molecular layer of the ChCl-2MA eutectic solvent to the four metal oxides. On the physical surface, a mineral–drug interaction model was established, and a certain vacuum layer was included to reduce the influence of periodic structure. The established interaction model was optimized, and kinetic calculations were carried out with the Forcite module [38,39]. During the calculation, the force field was COMPASSII, and the charge distribution was Forcefield-assigned. Furthermore, the calculation accuracy was set to ‘Fine’, and the electrostatic potential and van der Waals summing methods were the Ewald- and Atom-based, respectively. Various parameters, such as energy, temperature, and stable interaction model, were calculated using molecular dynamics, and the interaction energy and radial distribution function were calculated using the stable interaction model. Thus, the interaction mechanism between ChCl-2MA and the four metal oxides was studied. Figure 4 shows the variations in energy and temperature in the molecular dynamics simulation of the four metal oxides and ChCl-2MA. In addition, Figure 5 shows the interaction model of the four metal oxides and that of ChCl-2MA, which were obtained using the simulation.

Figure 4. Cont.

Figure 4. Molecular dynamics simulation of different metal oxides with ChCl-2MA. Dynamic simulation of ChCl-2MA on ZnO (001) surface ((a): energy change (b): temperature change). Dynamic simulation of ChCl-2MA on Fe₂O₃ (001) surface ((c): energy change (d): temperature change). Dynamic simulation of ChCl-2MA on Al₂O₃ (001) surface ((e): energy change (f): temperature change). Dynamic simulation of ChCl-2MA on CaO (001) surface ((g): energy change (h): temperature change).

As can be seen from Figure 4, after the NVT ensemble simulation, the energy and temperature continuously changed. Finally, the energy of the interaction process between the four metal oxides and ChCl-2MA stabilized, and the range of the temperature variation was not large, indicating that the simulated system had reached a stable structure. Meanwhile, based upon the variations in energy, the total energy in the interaction process between ChCl-2MA and ZnO (001) was found to be low, and the total energy of the other three metal oxides was relatively high, which further shows that ChCl-2MA and ZnO (001) were more likely to react.

It can be seen from Figure 5 that the hydrogen bond of ChCl-2MA was broken during the interaction with ZnO (001), and the reactions took place on the upper and lower surfaces of ZnO (001). Moreover, Cl and O on the two MA molecules acted on the protruding surface of Zn, while choline cation acted on the protruding surface of O and formed C-H...O hydrogen bonds with it. Meanwhile, ChCl-2MA formed C-H...O and O-H...O hydrogen bonds during the interaction with Fe₂O₃ (001) and Al₂O₃ (001) surfaces. No hydrogen bond was observed between ChCl-2MA and CaO (001).

ChCl-2MA and ZnO (001) surface interaction model ((a): interaction before (b): interaction after); O: red, H: white, Zn: gray

ChCl-2MA and Fe₂O₃ (001) surface interaction model ((c): interaction before (d): interaction after); O: red, H: white, Fe: gray

ChCl-2MA and Al₂O₃ (001) surface interaction model ((e): interaction before (f): interaction after); O: red, H: white, Al: pink

ChCl-2MA and CaO (001) surface interaction model ((g): interaction before (h): interaction after); O: red, H: white, Ca: green

Figure 5. Interaction models of different metal oxides and ChCl-2MA.

3.2. Analysis of the Calculated Results

3.2.1. Interaction Energy

The interaction energy is calculated using the correlation: $\Delta E = E_{AB} - E_A - E_B$, where ΔE is the interaction energy of the eutectic solvent and metal oxide after interaction, and E_{AB} , E_A , and E_B are the total energy of the interaction model, the metal oxide, and the eutectic solvent, respectively. With decreasing interaction energy, the stability of the adsorption increases, and vice versa [40]. The results presented in Table 4 outline the calculated interaction energies between the complete-cleavage surfaces of the four metal oxides and ChCl-2MA.

Table 4. Interaction energies between the complete-cleavage surfaces of the metal oxides and ChCl-2MA (/eV).

Complete-Cleavage Surface	E_A	E_B	E_{AB}	ΔE
ZnO(001)	6.3368	−10,983.7106	−11,015.7309	−38.3572
Fe ₂ O ₃ (001)	1.2463	−42,885.9960	−42,887.9668	−4.1929
Al ₂ O ₃ (001)	−9.2960	−13,7351.4606	−13,7364.4290	−3.6724
CaO(001)	−10.6916	−7373.6033	−7360.4413	−2.4703

The results presented in Table 4 show that the interaction energy between the ZnO (001) surface and ChCl-2MA was the smallest (−38.3572 eV), whereas the interaction between the four metal oxides and ChCl-2MA was indeed the strongest. Furthermore, the interaction energies of the three metal oxides and ChCl-2MA were relatively similar to each other, and the strength of the interaction was found to be in the following descending order: Fe₂O₃ (001) surface > Al₂O₃ (001) surface > CaO (001) surface.

3.2.2. Radial Distribution Function

The radial distribution function (RDF) indicates the spatial distribution probability of other particles centered on a given particle and is used to analyze the strength of the interaction between two substances. The peaks within 3.5 Å mainly indicate the existence of chemical bonds or hydrogen bonding between the substances. The peaks beyond 3.5 Å mainly indicate that the interaction between substances is Coulombic force or van der Waals force [41,42]. Figure 6 shows the atomic radial distribution of four metal oxides during the interaction with ChCl-2MA.

The results show that Cl in ChCl forms a chemical bond with Zn in ZnO. The Cl in ChCl interacts with the metal ions in the other three metal oxides by van der Waals forces. This can also be seen from the comparison of the density of the oxidation states of the four metals. Among the four metal oxides, the metal atom Zn is the most active, and the formed Cl-Zn chemical bond exhibited strong bond energy. The chemical bond between O in MA and the metal atoms in the four metal oxides was weak because the O in the metal oxide forms strong chemical bonds with the metal atoms. By comparing the initial peak position and peak strength, it is found that the hydrogen bond strength formed by interaction with three metal oxides decreases in the order Al₂O₃ > ZnO > Fe₂O₃, and the interaction between ChCl-2MA and CaO was mainly based on van der Waals force. It can be concluded that the interaction between ChCl and MA and ZnO is dominated by chemical action and supplemented by physical forces. The interactions between ChCl-2MA and the other three metal oxides (Fe₂O₃, Al₂O₃, and CaO) are mainly physical. The analysis of the radial distribution function shows that the strength of the interaction between ChCl-2MA and the four metal oxides was consistent with the calculation results of the interaction energy.

Figure 6. Radial distribution diagram of mineral adsorption model. ZnO (001) surface and ChCl-2MA radial distribution (a): Cl-Zn distance (b): O-Zn distance (c): O₁-H distance. Fe₂O₃ (001) surface and ChCl-2MA radial distribution (d): Cl-Fe distance (e): O-Fe distance (f): O₁-H distance. Al₂O₃ (001) surface and ChCl-2MA radial distribution (g): Cl-Al distance (h): O-Al distance (i): O₁-H distance. CaO (001) surface and ChCl-2MA radial distribution (j): Cl-Ca distance (k): O-Ca distance (l): O₁-H distance.

4. Model Verification and Analysis

4.1. Experimental Materials and Methods

The particle size of ZnO, Fe₂O₃, Al₂O₃, and CaO used in the experiment was 0.106–0.155 mm, and the purity was greater than 99%. Each leaching experiment was carried out with a total sample amount of 5.00 g. ChCl and MA used in this study were analytically pure. First, ChCl and MA were mixed in a molar ratio of 1:2. The mixture was stirred in a beaker and placed in a vacuum drying oven at 80 °C under −0.05 MPa for 12 h until the solids dissolved into a uniform transparent solution, which indicated that ChCl-2MA DES was formed. The leaching effects of ChCl-2MA were determined for the four metal oxides under various leaching temperatures, liquid–solid ratios, and leaching periods.

4.2. Single Mineral Leaching Experiment

The accuracy of the simulation results was verified using the ChCl-2MA leaching experiment for the four metal oxides. The leaching amounts of the four metal oxides for three different leaching parameters are displayed in Figure 7. The calculated results of the leaching were within an error of 2%. Figure 7a shows the leaching rate as a percentage at various temperatures and a fixed leaching time of 15 min and a liquid-to-solid ratio of 10:1. In Figure 7b, the leaching rate is plotted over the leaching time at a fixed leaching temperature of 70 °C and a liquid-to-solid ratio of 10:1. The liquid-to-solid ratio is varied in Figure 7c at a fixed leaching time of 15 min and a leaching temperature of 70 °C.

Figure 7. Leaching rates of metal oxides under different leaching conditions. (a): Leaching rates at different temperatures. (b): Leaching rates at different times. (c): Leaching rate of different liquid solid ratio.

According to Figure 7a, the leaching of ZnO by ChCl-2MA varied greatly with different leaching temperatures. The leaching rate amounted to 45.21% at 50 °C and increased continuously to 93.48% at 90 °C. The leaching for the other three metal oxides did not change much with the change in temperature and remained stable at about 10%. At 90 °C, the highest leaching rate for the three metal oxides was observed with values of 14.23% for Fe₂O₃, 10.23% for Al₂O₃, and 9.04% for CaO. It can be seen from Figure 7b,c that, with the increase in leaching time and liquid-to-solid ratio, the leaching of ZnO by ChCl-2MA increased and, finally, reached a stable value, while the leaching of the other metal oxides showed little variation with the change in leaching time. The results show that, among various independent variables, the effect of leaching temperature was far stronger for ZnO than for the other three metal oxides.

5. Conclusions

- (1) The optimal structural parameters of the four metal oxides were obtained by calculating their exchange-correlation energy functionals. Moreover, the complete-cleavage surfaces were calculated, and those with the lowest surface energy were found to be the (001) surfaces for all metal oxides. The optimized stable configuration of ChCl-2MA features multiple intermolecular hydrogen bonds with the chlorine atom as the center.

- (2) A comparative analysis of the cell and complete-cleavage surfaces density of the four metal oxides shows that the ZnO (001) surface near the Fermi level receives a higher contribution from the Zn-3d orbital than the O-2p orbital. The Fe₂O₃ (001) surface near the Fermi level is contributed by Fe-3d and O-2p orbitals, and their activities are similar. The increase in the total density of states of the Al₂O₃ (001) surface is mainly due to the increase in the density of states of the O-2p orbital, indicating that the O-2p orbital is more likely to react with foreign substances. The peak density of states of the CaO (001) surface near the Fermi level is mainly contributed by the O-2p orbital, indicating that O is more likely to react with foreign substances in the complete-cleavage surface of CaO.
- (3) It can be seen from the energy change determined by molecular dynamics that ChCl-2MA is more likely to interact with the ZnO (001) surface. The variation in energy shows that ChCl-2MA is more inclined to interact with ZnO (001). The results also show that the interaction between ZnO and ChCl-2MA is the strongest, and the interaction of the metal oxides with ChCl-2MA decreases in the following order: ZnO > Fe₂O₃ > Al₂O₃ > CaO.
- (4) Based on the analysis of the radial distribution function, it is inferred that the Cl in ChCl forms a chemical bond with Cl-Zn, whereas Cl interacts with Fe, Al, and Ca through van der Waals forces. The chemical bond of Cl is stronger than that formed by Zn. The chemical bond between O in MA and metal atoms is weak. By comparing the initial peak position and the peak intensity, it is found that the strength of the hydrogen bond formed by the interaction between ChCl-2MA and the three metal oxides follows the descending order: Al₂O₃ > ZnO > Fe₂O₃. Moreover, the interaction between ChCl-2MA and CaO is mainly based on van der Waals forces.
- (5) The leaching rate of the four metal oxides by ChCl-2MA was experimentally determined under different conditions for three leaching parameters. It is found that the leaching of ZnO by ChCl-2MA reaches more than 90%, while the leaching for the other three metal oxides remains stable at about 10%. These results verify the accuracy of the molecular simulation and also prove that ChCl-2MA is selective for ZnO in zinc-bearing dust sludge.

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