

# New atomic scale simulation models for hydroxides and oxyhydroxides

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This work has three aims. First to review the significance of hydroxide containing systems to materials science. Second to report two consistent and transferable sets of interatomic potentials that facilitate the atomic scale modelling of such systems. The first set of potentials is based on the assumption that ions adopt their full formal charge states, the second model assumes that partial charges are more realistic. The third aim is use the models to predict the structures of an extensive set of oxides, hydroxides, and oxyhydroxides. The predictions are compared with experimental results and previous computational studies. Both potential sets yield excellent agreement with the experimental data. A feature of the interatomic potential sets is the use of a screened Coulombic potential to describe the oxygen-hydrogen interaction at short distances rather than the more widely used Coulomb-subtracted Morse potential. The potential sets are discussed in the context of the new structures and processes that they can be employed to model. © 2006 Springer Science + Business Media, Inc.

## 1. Introduction

Whenever a material comes into contact with the natural environment there is an interaction with water (liquid or vapour). For many metals and ceramics this takes the form of a chemical reaction in which a hydroxide or oxyhydroxide is formed. If the reaction proceeds to completion there is a new bulk phase but often the reaction is kinetically hindered and only a surface or passive layer is formed.

From both crystallographic and bonding points of view these materials form an extensive and diverse set of compounds. It is therefore a significant challenge to derive a single consistent set of potentials that are able to reproduce a multitude of such structures to a good degree of accuracy. The aim of this paper is to report two internally consistent transferable atomic scale models that are able to do just that. The hydroxides modelled are:  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ,

$\text{Y}(\text{OH})_3$ ,  $\text{Sc}(\text{OH})_3$ ,  $\text{In}(\text{OH})_3$ ,  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ , and most of their polymorphs. The oxyhydroxides to be considered are:  $\text{FeO}(\text{OH})$ ,  $\text{AlO}(\text{OH})$ ,  $\text{CrO}(\text{OH})$ ,  $\text{ScO}(\text{OH})$ ,  $\text{InO}(\text{OH})$  and their polymorphs. Given the incorporation of  $\text{O}^{2-}$  in the oxyhydroxide structures, the potential parameters were also derived through comparison to the corresponding oxides:  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ , and  $\text{Sc}_2\text{O}_3$ . The use of interatomic potentials to model oxides is well established (see for example, [1–3]) and the structures well known, thus we will not report on these here.

Details of the potential models used in this study are given in part 2, and the crystal structures of the hydroxides and oxyhydroxides considered in this work are described in part 3. Detailed comparison between experimental data, previous simulations and the present results will be made in part 3 as well. First, however, the rationale behind the selection of these materials is discussed.

Certainly many of these materials are of technological significance. For example, a number of the iron containing systems are products of ferrous alloy corrosion. However, the structures of the layers developed during, for example, aqueous corrosion are multiphase and nano-crystalline, even on well orientated metal surfaces under well controlled conditions [4]. For most engineering materials the corrosion process is, of course, not well defined and it results in the formation of additional non-equilibrium phases. Of particular importance are metastable FeO(OH) phases such as goethite and akaganeite, which are formed by re-precipitation of dissolved Fe<sup>3+</sup> and lepidocrocite which forms through oxidation of Fe<sup>2+</sup> containing solutions [5]. Many of these phases are therefore only observed under specific circumstances. Fe(OH)<sub>2</sub>, for example, requires reducing conditions in order to form [6, 7] and while it is subsequently unstable as a pure phase, it can be stabilized once as little as 10% of the Fe<sup>2+</sup> is substituted by Fe<sup>3+</sup> [8].

Cation substitution is also of interest in iron containing soil minerals such as goethite and its decomposition product hematite (or haematite), where the substitution of Al<sup>3+</sup> at Fe<sup>3+</sup> sites results in significant changes to crystallite morphology [9]. Not surprisingly soil colour is related to the types and amount of iron mineral content but it also depends on crystallite size and shape [10]. Interestingly there is a considerable difference in the extent of dopant ion solubility between different FeO(OH) polymorphs [5].

The iron containing mineral content in soil also has an environmental significance as it is these phases that act as traps for heavy metal ions (e.g. lead and cadmium) and for other harmful species (e.g. arsenic, toxic organics and phosphates) [5]. Industrially this effect is used for water purification by precipitating iron minerals in situ that remove the afore mentioned contaminants [11]. In these cases it is mineral surfaces that provide the active sites and availability will depend on crystallite morphology. Finally, iron containing minerals have been found in a variety of organisms. These bio-minerals include goethite, lepidocrocite and magnetite, the latter reportedly functioning as a navigational device [12].

Equivalent comments to those made above about materials that contain iron could be made about materials that contain aluminium. Geologically three stable polymorphs of Al(OH)<sub>3</sub> exist, gibbsite, bayerite and nordstrandite all of which are commonly present in the form of fine-grains in consolidated sediments and sedimentary rocks [13]. Gibbsite is industrially important because of its role in alumina production [14]. It is a common mineral since it is one of the constituents of bauxite, which is the raw material for the extraction of aluminium via the Bayer process [15]. Bayerite is of commercial significance since it is an undesirable product of the Bayer process for the extraction of aluminium [15].

For corrosion of aluminium under atmospheric or certain aqueous conditions, thin films of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> form, which are usually very adhesive and therefore highly protective. Under very low or high pH conditions, however, aqueous corrosion will proceed, giving rise to the formation of complex films that include, for example, polymorphs of Al(OH)<sub>3</sub> [16]. Unfortunately, pure aluminium is of little use and alloying additions, particularly copper, have a detrimental effect on corrosion resistance as they form precipitates (the mechanical hardening mechanism) which leads to localized corrosion [17]. Protection of alloys can be provided through electrochemically forming a protective layer such as lithium hydrotalcite LiAl<sub>2</sub>(OH)<sub>6</sub>OH·2H<sub>2</sub>O [18, 19].

Alkaline earth metal hydroxides are also of technological significance. Portlandite, Ca(OH)<sub>2</sub>, in particular is a major component of hydrated Portland cement [20]. It is, however, the mixed cation cement phases that would be of most interest to model. Atomic scale simulation has already been successful in modelling some such phases, in particular, the refractory components of cement such as Ca<sub>2</sub>FeAlO<sub>5</sub> brownmillerite (also known to the cement community as ferrite). In this case, it was possible to make useful predictions of disorder over the complete solid solution range Ca<sub>2</sub>Fe<sub>x</sub>Al<sub>2-x</sub>O<sub>5</sub> 0 < x < 2 [21] and also to predict the complex solution mechanisms for Ti<sup>4+</sup> ion substitution [1]. Finally, portlandite and brucite, Mg(OH)<sub>2</sub> are present in limited amounts in the earth's crust but are nevertheless considered to be potential sources of water in the mantle [22].

In short, there are a diverse selection of, industrially motivated incentives to develop better models for these classes of materials. This is a challenging prospect because the inter-atomic bonding includes semi-ionic covalent and hydrogen contributions. Certainly quantum mechanical approaches will be and have already been shown to be useful [14, 15, 23]. Nevertheless, here we have chosen to develop internally consistent full formal charge and partial charge models that demonstrate a high degree of transferability (for example, they reproduce the observed polymorphism). The motivation is to facilitate future studies of complex phenomena involving large numbers of ions and molecules. For example, it will be possible to develop models for the interfaces between different hydroxide, oxyhydroxide and oxide compounds that form during corrosion processes. Inter-atomic potentials are not likely to be useful for modelling the reaction processes, that will require a computationally intensive quantum mechanical approaches; however, empirically derived interatomic potentials can be used to model the broader structural evolution of configurations that arise from reaction processes and to model associated diffusional processes. It will also be possible to model the incorporation of isolated impurity defects and defect cluster formation within the different phases, at interlayer sites within intergrowth structures or

at surface specific sites [24]. As discussed above, such studies have important industrial and environmental applications.

## 2. Theoretical methods

### 2.1. Simulation technique

The modelling approach is based on the classical Born model description of the lattice [25]. Thus, the interaction between a pair of ions,  $E(r_{ij})$ , is given by,

$$E(r_{ij}) = \frac{q_i q_j}{r_{ij}} + S(r_{ij})$$

where the first term is the Coulomb interaction,  $S(r_{ij})$  represents the short range repulsive and van der Waals energies,  $r_{ij}$  is the separation between ions  $i$  and  $j$ , and  $q_i$  and  $q_j$  are the charges of the ions. The Coulombic forces are summed using Ewald's method [26], whereas the short-range forces are summed explicitly up to a cut-off value of 20 Å. For a given interatomic potential model, the lattice parameters and positions of ions within a given unit cell are identified through energy minimization. The atomistic simulation package GULP [27] was used throughout this study.

### 2.2. Partial charge and full charge models

The potential parameters for the full charge model were derived by assuming that the lattice ions assume their full charge states of  $-2.0 e$  for oxygen (where  $e$  is the electronic charge),  $+1.0 e$  for monovalent ions,  $+2.0 e$  for divalent ions and  $+3.0 e$  for trivalent ions. In the partial charge model the oxygen partial charge is  $-1.7 e$ , which is close to the centre of the values, predicted by Mulliken and Lowdin population analyses of periodic quantum mechanical calculations for oxides [28]. An oxygen charge of  $-1.7 e$  has been successfully used to predict the energies of systems as diverse as helium filled voids in MgO [29] and lattice disorder in complex rare earth pyrochlores [30].

### 2.3. Determination of short-range potential parameters

The short-range energy terms,  $S(r_{ij})$ , are approximated by a parameterized pair potential of the Buckingham form

$$S(r_{ij}) = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

where  $A_{ij}$ ,  $\rho_{ij}$  and  $C_{ij}$  are the potential parameters specific to ions  $i$  and  $j$ . Some of the oxide parameters for the full charge model used in this study were taken from previous work [31–33] in which the parameters were varied until a best fit to the experimental lattice parameters

TABLE I Buckingham interatomic potential parameters

Interaction	A (eV)	$\rho$ (Å)	C (eVÅ <sup>6</sup> )
(a) The full charge model			
O <sup>2.04-</sup> –O <sup>2.04-</sup>	9547.96	0.2192	32.0
O <sup>2.04-</sup> –O <sup>1.4-</sup>	10364.15	0.2373	22.6
O <sup>1.4-</sup> –O <sup>1.4-</sup>	15278.54	0.21922	16.0
O <sup>2.04-</sup> –H <sup>0.4+</sup>	591.35	0.2114	0.0
O <sup>1.4-</sup> –H <sup>0.4+</sup>	4220.76	0.10323	0.0
Na <sup>1.0+</sup> –O <sup>1.4-</sup>	1995.35	0.2731	5.2
Li <sup>1.0+</sup> –O <sup>1.4-</sup>	1424.24	0.2388	3.0
K <sup>1.0+</sup> –O <sup>1.4-</sup>	2650.24	0.295	12.0
Ca <sup>2.0+</sup> –O <sup>1.4-</sup>	1233.18	0.3131	0.0
Mg <sup>2.0+</sup> –O <sup>1.4-</sup>	685.91	0.3141	0.0
Fe <sup>2.0+</sup> –O <sup>1.4-</sup>	886.91	0.3050	0.0
Fe <sup>3.0+</sup> –O <sup>1.4-</sup>	2304.60	0.2738	0.0
Fe <sup>3.0+</sup> –O <sup>2.04-</sup>	1199.5	0.3254	0.0
Al <sup>3.0+</sup> –O <sup>1.4-</sup>	2631.42	0.2527	0.0
Al <sup>3.0+</sup> –O <sup>2.04-</sup>	1361.29	0.3013	0.0
Sc <sup>3.0+</sup> –O <sup>1.4-</sup>	2598.40	0.2742	0.0
Sc <sup>3.0+</sup> –O <sup>2.04-</sup>	1575.85	0.3211	0.0
Cr <sup>3.0+</sup> –O <sup>1.4-</sup>	2291.40	0.2704	0.0
Cr <sup>3.0+</sup> –O <sup>2.04-</sup>	1204.18	0.3165	0.0
In <sup>3.0+</sup> –O <sup>1.4-</sup>	1188.42	0.3160	0.0
In <sup>3.0+</sup> –O <sup>2.04-</sup>	1495.65	0.3327	0.0
Y <sup>3.0+</sup> –O <sup>1.4-</sup>	1248.42	0.3360	0.0
(b) The partial charge model			
O <sup>2.23-</sup> –O <sup>2.23-</sup>	487936.0	0.182	47.0
O <sup>2.23-</sup> –O <sup>2.05-</sup>	18535.73	0.2101	39.0
O <sup>2.05-</sup> –O <sup>2.05-</sup>	14390.18	0.2282	28.0
O <sup>2.23-</sup> –H <sup>0.35+</sup>	591.35	0.2114	0.0
O <sup>2.05-</sup> –H <sup>0.35+</sup>	4020.15	0.101	0.0
Na <sup>0.85+</sup> –O <sup>2.05-</sup>	1557.47	0.2725	0.0
Li <sup>0.85+</sup> –O <sup>2.05-</sup>	1196.53	0.2342	0.0
K <sup>0.85+</sup> –O <sup>2.05-</sup>	1966.70	0.2940	0.0
Ca <sup>1.7+</sup> –O <sup>2.05-</sup>	997.30	0.31325	0.0
Mg <sup>1.7+</sup> –O <sup>2.05-</sup>	529.70	0.3142	0.0
Fe <sup>1.7+</sup> –O <sup>2.05-</sup>	708.60	0.29992	0.0
Fe <sup>2.55+</sup> –O <sup>2.05-</sup>	1961.93	0.2655	0.0
Fe <sup>2.55+</sup> –O <sup>2.23-</sup>	1014.70	0.3190	0.0
Al <sup>2.55+</sup> –O <sup>2.05-</sup>	2111.50	0.251	0.0
Al <sup>2.55+</sup> –O <sup>2.23-</sup>	1035.75	0.29032	0.0
Sc <sup>2.55+</sup> –O <sup>2.05-</sup>	1966.30	0.2751	0.0
Sc <sup>2.55+</sup> –O <sup>2.23-</sup>	1125.27	0.3208	0.0
Cr <sup>2.55+</sup> –O <sup>2.05-</sup>	1944.56	0.2751	0.0
Cr <sup>2.55+</sup> –O <sup>2.23-</sup>	972.74	0.3070	0.0
In <sup>2.55+</sup> –O <sup>2.05-</sup>	995.00	0.3130	0.0
In <sup>2.55+</sup> –O <sup>2.23-</sup>	1193.34	0.3253	0.0
Y <sup>2.55+</sup> –O <sup>2.05-</sup>	1003.28	0.3283	0.0

and atomic positions was achieved. The same approach has been employed here to expand the set of potentials to include ionic species required for modelling hydroxides and oxyhydroxides. The optimal values of potential parameters for the full charge model are reported in Table Ia and the best values for the partial charge model are given in Table Ib.

### 2.4. Derivation of the O–H potential model

The potential model used to describe the interactions between atoms of the hydroxyl group must take into account

the strong degree of overlap between these species due to the short interatomic separation of about 1 Å. At such small separations, pure Coulombic forces are too large to accurately describe the interactions between oxygen and hydrogen. A popular way of describing the interactions within and between hydroxyl groups is to employ a Coulomb-subtracted Morse potential at bonded separations and a Buckingham potential at non-bonded separations. This has proved highly successful in many cases [14, 24] but problems can arise if O–H separations are close to the cut-off point between the two potential types, which can be a particular problem in defective materials. For this reason, we have developed a ‘screened Coulombic potential’ to be used simultaneously with the Buckingham potential. The form of the screened Coulombic potential is

$$V(r_{\text{OH}}) = \frac{q_{\text{O}}q_{\text{H}}}{4\pi\epsilon_0 r_{\text{OH}}} \left[ 1 - \exp\left(-\frac{r_{\text{OH}}}{\rho}\right) \right]$$

where the electrostatic interaction between the oxygen and hydrogen atoms decreases exponentially as the ionic separation is decreased. The screening term has negligible effect at separations larger than 1.5 Å, where O–H overlap is greatly reduced. It can therefore be included in calculations of interactions between non-bonded hydrogen and oxygen atoms i.e. only one potential model is used. The  $\rho$  parameter has a value of 0.479177 Å for both the full and the partial charge model.

### 2.5. The shell model for polarisability

The oxygen ions are treated as polarisable by virtue of the shell model [34], in which a polarisable ion is comprised of a charged spherical shell and a charged core which are connected via an isotropic harmonic spring. In the full charge model, the  $\text{O}^{2-}$  ions have a shell charge of  $-2.04$  e, a core charge of  $+0.04$  e and a force constant of  $6.3$  eV Å<sup>-2</sup>. The oxygen ion that is bound to a hydrogen ion has a shell charge of  $-2.3$ e, a core charge of  $+0.9$  e, and a force constant of  $75.57$  eV Å<sup>-2</sup>. The hydrogen has a charge of  $+0.4$  e and does not have a shell; the net charge of a hydroxyl group is therefore  $-1.0$  e. In the partial charge model, the  $\text{O}^{1.7-}$  ions have a shell charge of  $-2.23$  e, a core charge of  $+0.53$  e and a force constant  $32.0$  Ev. Oxygen ions that are bound to hydrogen ions have a shell charge of  $-2.05$  e, a core charge of  $+0.85$  e, and a force constant of  $60.04$  eV Å<sup>-2</sup>. Hydrogen has a charge of  $0.35$  e, again without a shell, so that the net charge a hydroxyl group in the partial charge model is  $-0.85$  e. For both full and partial charge models, although the pair potential parameters were derived with the shell model (and thus the predictions are closer to experiment when the shell model is included), most work adequately without the inclusion of the shell.

## 3. Results and discussion

### 3.1. Portlandite and brucite

Many experimental structural determinations of  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  have been carried out [22, 35–46] giving a small range of lattice parameters but a very consistent cation–oxygen bond length in each case. Theoretical structural investigations have also been made, particularly in the case of brucite [14, 47–52]. One reason for such interest is the nature of the bonding between hydroxyl layers, with some studies concluding that hydrogen bonding is present, and others finding evidence of stronger interactions.

$\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  are isostructural and exhibit the  $\text{CdI}_2$  type structure (space group  $P\bar{3}m1$  No. 164). In this, layers of hydroxyl groups along the  $c$ -direction separate planar hexagonal stacks of Ca (or Mg). There is one formula unit per unit cell and the Ca or Mg atoms lie in invariant positions (0,0,0) while the O and H atoms are located in the positions  $\pm(1/3, 2/3, Z_{\text{O}})$  and  $\pm(1/3, 2/3, Z_{\text{H}})$ . Portlandite and brucite can also be described as layered structures formed by stacking (0 0 1) sheets of edge sharing  $\text{MO}_6$  octahedra.

The predictions for lattice parameters, cation–O distances and O–H distances for  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  are compared with experimental [22, 35–46] and previous computational studies [14, 47–52] in Table IIA and B (note: distances are calculated between the oxygen core and hydrogen or oxygen core and cation in all cases). The volume per unit cell of portlandite is predicted to 0.1% and for brucite to 1% of the mean experimental values. The partial-charge model Ca–O distance is closer to the experimental values compared not only to the full charge model but also to the other theoretical studies. In both structures the O–H bond length predicted by both models falls within the range of experimental values but values predicted by the other theoretical studies are, in general, a little longer. A possible explanation of this is that in experimental X-ray studies the O–H distance appears shorter because of the concentration of the electron density in the bond as opposed to the hydrogen nucleus [53].

### 3.2. Iron hydroxides and oxyhydroxides

There are limited experimental studies of the structures of divalent and trivalent iron hydroxides. While iron hydroxide,  $\text{Fe}(\text{OH})_2$ , is isostructural with portlandite and brucite it has been subject to far fewer structural investigations [54]. Thus, although the predicted values are in good agreement with the experimental value (Table IIC), the propensity for this material to oxidize must cast some doubt on the experimental data and further studies would be welcome.

Bernalite,  $\text{Fe}(\text{OH})_3$ , is orthorhombic (space group  $\text{Immm}$  No. 71) [55] and resembles the distorted perovskite structure of the rare earth orthoferrites [56]. The



TABLE IIA The experimentally determined and calculated structure of portlandite

	$a$ (Å)	$c$ (Å)	$d(\text{Ca-O})$ (Å)	$d(\text{O-H})$ (Å)
Space group $P\bar{3}m1$ Portlandite $\text{Ca}(\text{OH})_2$				
Experimental data				
Busing (1957) 133 K	3.5862	4.8801	2.366	0.984
Petch (1961)	3.5853	4.895	–	0.79
Henderson (1962) 83 K	3.585	4.874	2.361	0.99
Chaix-Pluchery (1987) RT	3.5918	4.9063	2.370	0.987
Desgranges (1993) RT	3.589	4.911	2.371	0.95
Pavese (1997)	3.5851	4.9035	–	0.92
Simulated structures				
LeSar (1982)	3.681	4.837	–	0.982
Fleming (2000)	3.57	4.94	2.44	0.981
Cygan (2004)	3.693	4.796	2.515	1.023
Full charge model	3.519	5.102	2.306	0.960
Partial charge model	3.575	4.952	2.348	0.968

TABLE IIB The experimentally determined and calculated structures of Brucite

	$a$ (Å)	$c$ (Å)	$d(\text{Mg-O})$ (Å)	$d(\text{O-H})$ (Å)
Space group $P\bar{3}m1$ Brucite $\text{Mg}(\text{OH})_2$				
Experimental data				
Zigan (1967)	3.142	4.766	2.102	0.995
Černý (1995)	3.1477	4.7717	2.096	1.007
Catti (1995)	3.14979	4.7702	2.1003	0.958
Desgranges (1996) 70 K	3.145	4.740	2.092	0.957
Desgranges (1996) 0 K	3.148	4.779	2.097	0.956
Zhukhlistov (1997)	3.149	4.769	2.100*	0.945*
Nagai (2000)	3.1425	4.7665	2.0954	–
Simulated structures				
LeSar (1982)	3.221	5.051	–	0.982
D'Arco (1993)	3.146	5.354	2.103	0.953
Winkler (1995)	3.13	4.71	2.083	0.946
Baram (1996)	3.0853	4.5895	2.013	1.026
Fleming (2000)	3.10	4.76	2.154	0.991
Chizmeshya (2002)	3.149	4.752	2.116*	0.979*
Full charge model	3.135	4.779	2.079	0.958
Partial charge model	3.168	4.710	2.111	0.965

\*These distances were derived from the atomic coordinates.

mineral bernalite is unstable and it commonly coexists with goethite,  $\alpha\text{-FeO}(\text{OH})$ , which is its decomposition product [56]. On the face of it, modelling the structure of bernalite,  $\text{Fe}(\text{OH})_3$ , is difficult because of the absence of hydrogen positions, the fractional occupancy of the iron and oxygen atoms in the experimental results and the stated presence of water in the experimental specimen. Since our model does not include water, we are forced to assume a pure hydroxide. Nevertheless, the predicted Fe–O distance is within the range of the experimental results (Table IID). Although further modelling work on this system is necessary before a definitive statement can be made, the present results show that it is not necessary to invoke the presence of water molecules.

TABLE IIC The experimentally determined and calculated structures of  $P\bar{3}m1$   $\text{Fe}(\text{OH})_2$ 

	$a$ (Å)	$c$ (Å)	$d(\text{Fe-O})$ (Å)	$d(\text{O-H})$ (Å)
Space group $P\bar{3}m1$ $\text{Fe}(\text{OH})_2$				
Experimental data				
Natta (1928)	3.25	4.48	2.2084*	–
Full charge model	3.190	4.797	2.111	0.959
Partial charge model	3.177	4.700	2.116	0.965

\*These distances were derived from the atomic coordinates.

TABLE IID The experimentally determined and calculated structures of Bernalite

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$d(\text{Fe-O})$ (Å)	$d(\text{O-H})$ (Å)
Space group Immm Bernalite $\text{Fe}(\text{OH})_3$					
Experimental data					
Birch (1993)	7.544	7.560	7.588	1.984–2.035	–
Full charge model	7.736	7.736	7.736	1.994	0.971
Partial charge model	7.736	7.736	7.736	1.994	0.977

There are three polymorphs of iron oxyhydroxide,  $\text{FeO}(\text{OH})$ : goethite, akaganeite and lepidocrocite. Goethite,  $\alpha\text{-FeO}(\text{OH})$ , is orthorhombic (space group  $Pnma$  No. 62) and is isostructural with  $\text{AlO}(\text{OH})$  (diaspore),  $\text{CrO}(\text{OH})$  (bracwellite) and  $\text{ScO}(\text{OH})$  [57]. Goethite is the most stable iron oxyhydroxide [58] and consists of double bands of octahedra, which are linked at their corners by sharing oxygen ions, to form  $2 \times 1$  octahedra tunnels. Akaganeite,  $\beta\text{-FeO}(\text{OH})$ , is tetragonal (space group  $I4/m$  No. 87). The crystal structure of lepidocrocite,  $\gamma\text{-FeO}(\text{OH})$ , was determined to be  $\text{Cmcm}$  by X-ray diffraction methods [59] but was then refined in space group  $\text{Cmc}2_1$  (No. 36) with the use of neutron powder diffraction methods [60]. In lepidocrocite, the double bands of octahedra share edges and form zigzag layers, which are connected to each other by hydrogen bonds. Therefore,  $\gamma\text{-FeO}(\text{OH})$ , is orthorhombic and isostructural with  $\text{AlO}(\text{OH})$  (boehmite). The full charge model provides a superior fit for most iron oxyhydroxides, particularly goethite (Table IIE–G). The O–H distances are within the experimental range of values [57, 60–68] apart from the case of goethite, which is overestimated when compared to experiment but underestimated when compared to previous modelling work [53, 69, 70]. The fact that a single set of potentials can reproduce all three polymorphs is clearly encouraging.

### 3.3. Aluminium hydroxides and oxyhydroxides

The common polymorphs of  $\text{Al}(\text{OH})_3$  are gibbsite, bayerite and nordstrandite. The structure of a fourth rare  $\text{Al}(\text{OH})_3$  polymorph, doyleite, has been determined

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TABLE IIE The experimentally determined and calculated structure of goethite

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$d(\text{Fe-O})$ (Å)	$d(\text{O-H})$ (Å)
Space group Pnma Goethite $\alpha$ -FeO(OH)					
Experimental data					
Szytula (1968)	9.95	3.02	4.62	1.95–2.09	0.88
Hazemann (1992)	9.9528	3.0236	4.6188	1.954–2.068*	–
Majzlan (2003a)	9.9550	3.0224	4.6089	–	–
Simulated structures					
Rustad (1996)	10.03	3.14	4.85	2.09	0.99
Jones (2000)	9.94	3.07	4.56	–	–
Rosso (2001)	9.80	3.00	4.49	1.97–2.07	1.05
Full charge model	9.791	3.138	4.577	2.062	0.981
Partial charge model	9.268	3.146	4.704	2.074	0.984

\*These distances were derived from the atomic coordinates.

TABLE IIF The experimentally determined and calculated structure of akaganeite

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$d(\text{Fe-O})$ (Å)	$d(\text{O-H})$ (Å)
Space group I4/m Akaganeite $\beta$ -FeO(OH)					
Experimental data					
MacKay (1960)	10.44	10.44	3.03	2.01–2.20	–
Szytula (1970)	10.44	10.44	3.03	1.86	–
Post* (1991)	10.61	10.51	3.03	2.32	0.93–1.03
Simulated structures					
Rustad (1996)	10.84	10.84	3.13	2.28	–
Rosso (2001)	10.38	10.37	3.01	1.93–2.11	0.98
Full charge model	10.295	10.295	3.126	2.083	0.956
Partial charge model	10.145	10.145	3.138	2.072	0.961

\*Space group I2/m.

TABLE IIG The experimentally determined and calculated structure of lepidocrocite

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$d(\text{Fe-O})$ (Å)	$d(\text{O-H})$ (Å)
Space group Cmc Lepidocrocite $\gamma$ -FeO(OH)					
Experimental data					
Oles (1970)	3.06	12.51	3.87	1.974–2.135*	–
Christensen (1978)	3.08	12.50	3.87	1.913–2.116*	0.93
Christensen (1982)	3.07	12.53	3.88	1.97	0.78
Zhukhlistov (2001)	3.072	12.516	3.873	1.98–2.01	0.976*
Majzlan (2003b)	3.068	12.527	3.8699	–	–
Simulated structures					
Rustad (1996)	3.28	13.62	3.81	2.16	1.00
Jones (2000)	3.12	12.43	3.83	–	–
Rosso (2001)	3.01	12.19	3.86	1.97–2.06	1.05
Full charge model	3.167	12.548	3.702	2.032	1.008
Partial charge model	3.207	12.005	3.868	1.977	1.007

\*These distances were derived from the atomic coordinates.

recently [71]. Doyleite is triclinic (space group  $P\bar{1}$  No. 2) and closely resembles the structure of gibbsite, bayerite and nordstrandite apart from the hydrogen bonding between and within the layers [71]. Gibbsite (or hydrargillite) is a layered structure that crystallizes in pseudo-hexagonal prisms with monoclinic symmetry (space group  $P2_1/n$  No. 14) [72, 73] although it has also been reported to crystallize with triclinic symmetry [74]. The hydroxyl groups of one layer are directly above the hydroxyl groups of the neighbouring layer [75]. Bayerite

(space group  $P2_1/a$  No. 14) has a pseudo-trigonal layer structure in which the oxygen atoms form hexagonally close pack of spheres [76]. The oxygen-oxygen distances are shorter near Al atoms and the O–Al–O stacking resembles gibbsite [76]. Nordstrandite is the less common crystalline form of  $\text{Al}(\text{OH})_3$  and shares a space group with doyleite [75, 77].

There are also three polymorphs of  $\text{AlO}(\text{OH})$ : diaspore, boehmite and a newly reported tetragonal  $\delta$ - $\text{AlO}(\text{OH})$  phase [78]. The latter phase (space group  $\text{Pmn}21$  No. 31)

TABLE I(H) The experimentally determined and calculated structure of bayerite

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$d(\text{Al-O})$ (Å)	$d(\text{O-H})$ (Å)
Space group $P2_1/a$ Bayerite $\text{Al}(\text{OH})_3$					
Experimental data					
Rothbauer (1967)	5.062	8.671	4.713	1.738–2.059*	0.977*
Simulated structures					
Fleming (2000)	5.06	8.81	4.745	–	–
Gale (2001) PBE/PBE	5.107	8.852	4.7585	–	–
Gale (2001) LBS	5.149	8.915	4.711	–	–
Full charge model	5.082	8.635	4.937	1.894	0.950**
Partial charge model	5.070	8.790	4.966	1.925	0.973**

\*These distances were derived from the atomic coordinates.

\*\*Mean O-H distance.

TABLE II(I) The experimentally determined and calculated structure of gibbsite

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$d(\text{Al-O})$ (Å)	$d(\text{O-H})$ (Å)
Space group $P2_1/n$ Gibbsite $\text{Al}(\text{OH})_3$					
Experimental data					
Megaw (1961)	8.641	5.0704	9.719	–	–
Saalfeld (1974)	8.684	5.078	9.736	1.903	0.864
Simulated structures					
Baram (1996)	8.7934	5.1223	10.1539	–	–
Teppen (1997)	8.77	5.08	9.70	1.9	0.970
Fleming (2000)	8.81	4.99	9.79	–	–
Gale (2001) LDA/LDA	8.504	4.867	9.224	–	0.981*
Gale (2001) LDA/PBE	8.623	5.017	9.598	–	0.981*
Gale (2001) PBE/PBE	8.798	5.11	9.674	–	0.981*
Gale (2001) LBS	8.887	5.171	9.696	–	0.981*
Full charge model	8.745	5.021	9.663	1.886	0.961*
Partial charge model	8.740	5.108	9.968	1.915	0.966*

\*Mean O-H distance.

was synthesized at 21 GPa and 1000 °C and is isostructural with  $\text{InO}(\text{OH})$  [78]. As mentioned above, boehmite is isostructural with  $\gamma\text{-FeOOH}$ . Diaspore is isostructural to  $\alpha\text{-FeO}(\text{OH})$  [79, 80].

The transferability of the new potential models among the aluminium containing polymorphs was tested by fitting was tested fitting to 4 hydroxides (Table IIIH–K) and 3 oxyhydroxides (Table IIIL–N). Both potential models predict that the Al–O and O–H distances are the same in doyleite and nordstrandite; however, the limited structural experimental data [71, 77] for these structures preclude further evaluation of the models. Bayerite and gibbsite have been studied more extensively experimentally [72, 76, 81] and theoretically [14, 15, 50, 82]. For all aluminium hydroxides the full and partial charge model describe the lattice parameters to a similar degree of accuracy and better than some of the previous theoretical studies. This is also the case for the  $\delta\text{-AlO}(\text{OH})$  phase [78]. For diaspore and boehmite the full charge model agrees with the experimental [57, 65, 83–87] and computational [49, 52, 70, 88, 89] data better than the partial charge model.

### 3.4. Scandium, indium and yttrium hydroxides

The principle reason for modelling the tri-hydroxides of Y, In and Sc was to broaden the range of trivalent cation radii available for future studies of cation substitution.  $\text{Y}(\text{OH})_3$  is hexagonal (space group  $P6_3/m$  No.176) with two formula units per unit cell [90].  $\text{In}(\text{OH})_3$  is cubic (space group  $\text{Im}\bar{3}$  No. 204) and isostructural with  $\text{Sc}(\text{OH})_3$  [91].

Both the full and the partial charge models predict the experimental structural parameters of scandium [92] and indium [91, 93] tri-hydroxides accurately (Table II O and P). The partial charge model reproduces yttrium tri-hydroxide [90, 94] more effectively; however, the differences are not significant (Table II Q).

### 3.5. Scandium, indium and chromium oxyhydroxides

The two potential models were also used to study the oxyhydroxides of scandium, indium and chromium

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TABLE IIJ The experimentally determined and calculated structure of doyleite

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Al-O) (Å)	<i>d</i> (O-H) (Å)
Space group <i>P</i> $\bar{1}$ Doyleite Al(OH) <sub>3</sub>					
Experimental data					
Rodgers (1998)	4.9997	5.1681	4.9832	1.909*	0.96*
Full charge model	5.039	5.050	5.002	1.89	0.957**
Partial charge model	5.080	5.186	5.053	1.922	0.967**

\*These distances were derived from the atomic coordinates.

\*\*Mean O-H distance.

TABLE IIK The experimentally determined and calculated structures nordstrandite

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Al-O) (Å)	<i>d</i> (O-H) (Å)
Space group <i>P</i> $\bar{1}$ Nordstrandite Al(OH) <sub>3</sub>					
Experimental data					
Bosmans (1970)	5.082	5.127	4.980	2.01	–
Full charge model	5.089	5.050	5.003	1.89	0.957*
Partial charge model	5.129	5.186	5.053	1.922	0.967*

\*Mean O-H distance.

TABLE IIL The experimentally determined and calculated structure of diaspore

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Al-O) (Å)	<i>d</i> (O-H) (Å)
Space group <i>Pnma</i> Diaspore AlO(OH)					
Experimental data					
Hill (1979)	4.4007	9.4253	2.8452	1.9821	0.9886
Klug (1981)	4.4038	9.4284	2.8459	1.995*	0.990
Hazemann (1992)	4.4031	9.4252	2.8452	1.982*	–
Simulated structures					
Winkler** (1995)	4.401	9.421	2.845	1.966*	0.99
Rosso (2001)	4.29	9.26	2.80	1.85–1.92	1.06
Winkler (2001)	4.377	9.341	2.816	1.969	1.009
Digne (2002)	4.41	9.527	2.882	–	1.028
Full charge model	4.367	9.291	2.941	1.947	0.976
Partial charge model	4.480	8.564	2.897	2.020	0.969

\*These distances were derived from the atomic coordinates.

\*\*This author kept the lattice parameters fixed at the experimental values and only allowed the internal parameters to vary.

TABLE IIM The experimentally determined and calculated structure of boehmite

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Al-O) (Å)	<i>d</i> (O-H) (Å)
Space group <i>Cmc2</i> Boehmite AlO(OH)					
Experimental data					
Farkas (1977)	2.8684	12.2323	3.6949	1.85–2.01*	1.07*
Christoph (1979)	2.8679	12.214	3.6936	1.885–1.908*	–
Christensen (1982)	2.876	12.24	3.709	–	0.928
Bokhimi (2001)	2.851	12.12	3.736	1.81–2.16*	–
Simulated structures					
Rosso (2001)	2.82	11.82	3.63	1.85–1.95	1.04
Digne (2002)	2.904	12.069	3.744	–	1.020
Cygan (2004)	2.98	12.442	3.732	1.992	1.034
Full charge model	2.955	12.553	3.519	1.900	0.959
Partial charge model	3.141	12.331	3.322	1.886	0.973

\*These distances were derived from the atomic coordinates.

(bracewellite), again to increase further potential transference and to expand on the ionic species available for studies of cation substitution. ScO(OH) and CrO(OH) exhibit space group *Pnma* (No. 62) and are isostructural with goethite and diaspore [95, 96]. InO(OH) (space group

*Pmn*21 No. 31) is isostructural with  $\delta$ -AlO(OH) [78, 97, 98].

The structure of ScO(OH) [96] is reproduced more accurately with the full charge model (see Table IIR). Conversely InO(OH) [97, 98] is equally described by



TABLE IIN The experimentally determined and calculated structure of Pmn21 AlO(OH)

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Al-O) (Å)	<i>d</i> (O-H) (Å)
Space group Pmn21 $\delta$ -AlO(OH)					
Experimental data					
Suzuki (2000)	4.7134	4.2241	2.83252	1.83–2.03	–
Full charge model	4.546	4.323	2.891	1.799	1.027
Partial charge model	4.681	4.023	2.881	2.009	1.016

TABLE IIO The experimentally determined and calculated structure of Im $\bar{3}$  Sc(OH)<sub>3</sub>

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Sc-O) (Å)	<i>d</i> (O-H) (Å)
Space group Im $\bar{3}$ Sc(OH) <sub>3</sub>					
Experimental data					
Schubert (1948)	7.882	7.882	7.882	2.091*	–
Full charge model	7.881	7.881	7.881	2.036	0.970
Partial charge model	7.970	7.970	7.970	2.065	0.975

\*These distances were derived from the atomic coordinates.

TABLE IIP The experimentally determined and calculated structure of Im $\bar{3}$  dzhalindite In(OH)<sub>3</sub>

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (In-O) (Å)	<i>d</i> (O-H) (Å)
Space group Im $\bar{3}$ Dzhalindite In(OH) <sub>3</sub>					
Experimental data					
Christensen (1967a)	7.979	7.979	7.979	2.1828*	–
Mullica (1979)	7.9743	7.9743	7.9743	2.1606*	–
Full charge model	7.975	7.975	7.975	2.061	0.970
Partial charge model	8.105	8.105	8.105	2.103	0.974

\*These distances were derived from the atomic coordinates.

TABLE IIQ The experimentally determined and calculated structure of P6<sub>3</sub>/m Y(OH)<sub>3</sub>

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Y-O) (Å)	<i>d</i> (O-H) (Å)
Space group P6 <sub>3</sub> /m Y(OH) <sub>3</sub>					
Experimental data					
Christensen (1967b)	6.241	6.241	3.539	2.403*	0.9362
Beall (1977)	6.261	6.261	3.544	2.4091	0.8178
Full charge model	6.144	6.144	3.666	2.389	0.967
Partial charge model	6.161	6.161	3.632	2.404	0.974

\*These distances were derived from the atomic coordinates.

TABLE IIR The experimentally determined and calculated structure of Pnma ScO(OH)

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Sc-O) (Å)	<i>d</i> (O-H) (Å)
Space group Pnma ScO(OH)					
Experimental data					
Christensen (1967c)	4.755	10.301	3.209	1.969–2.059*	–
Full charge model	4.698	10.055	3.262	2.101	0.997
Partial charge model	4.781	9.628	3.261	2.140	0.986

\*These distances were derived from the atomic coordinates.

TABLE IIS The experimentally determined and calculated structure of bracewellite

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Cr-O) (Å)	<i>d</i> (O-H) (Å)
Space group Pnma Bracewellite CrO(OH)					
Experimental data					
Milton (1976)	4.492	9.860	2.974	1.930	–
Full charge model	4.486	9.624	3.053	2.042	0.973
Partial charge model	4.622	9.177	3.078	2.172	0.973

TABLE IIT The experimentally determined and calculated structure of Pmn21 InO(OH)

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (In-O) (Å)	<i>d</i> (O-H) (Å)
Space group Pmn21 InO(OH)					
Experimental data					
Christensen (1964)	5.26	4.56	3.27	2.1506*	–
Lehmann (1970)	5.26	4.56	3.27	2.1388*	–
Full charge model	5.150	4.538	3.333	2.213	1.037
Partial charge model	5.239	4.386	3.336	2.217	1.016

\*These distances were derived from the atomic coordinates.

the partial and full charge models (Table IIT). CrO(OH), however, is not so well reproduced with the calculated value of the *a*- lattice parameter significantly overestimated (as much as 8%) and the value of the *b*- lattice parameter noticeably underestimated (as much as 3%) compared with experimental values [95]. This arises from

an anisotropic crystal field distortion accompanying partially filled Cr<sup>3+</sup> d-orbitals [99], which is not included in the present model. This highlights one of the limitations of this type of isotropic inter-atomic potential model.

TABLE IIU The experimentally determined and calculated structure of LiOH

	<i>a</i> (Å)	<i>c</i> (Å)	<i>d</i> (Li-O) (Å)	<i>d</i> (O-H) (Å)
Space group P4/nmm LiOH				
Experimental data				
Dachs (1959)	3.557	4.339	1.9678	–
Mair (1978)	3.549	4.334	1.9632	0.936
Simulated structures				
LeSar (1982)	3.553	4.573	–	0.982
Full charge model	3.488	4.474	1.897	0.963
Partial charge model	3.546	4.184	1.930	0.970

TABLE IIV The experimentally determined and calculated structure of  $\alpha$ -NaOH

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Na-O) (Å)	<i>d</i> (O-H) (Å)
Space group Cmcm $\alpha$ -NaOH					
Experimental data					
Stehr (1967)	3.3994	11.377	3.3994	2.302*	0.917*
Bleif (1982)	3.401	11.382	3.401	2.322*	0.98
Jacobs (1985)	3.4013	11.378	3.3984	2.325*	0.931*
Simulated structures					
LeSar (1982)	3.44	11.775	–	3.44	0.982
Fleming (2000)	3.43	11.4	3.36	–	–
Full charge model	3.406	11.401	3.393	2.399	0.966
Partial charge model	3.463	11.255	3.442	2.437	0.974

\*These distances were derived from the atomic coordinates.

TABLE IIW The experimentally determined and calculated structure of  $\beta$ -NaOH

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Na-O) (Å)	<i>d</i> (O-H) (Å)
Space group P2 <sub>1</sub> /n $\beta$ -NaOH					
Experimental data					
Stehr (1967)	3.434	3.428	6.068	2.331*	1.149*
Bleif (1982)	3.435	3.445	6.080	2.373*	0.960
Full charge model	3.406	3.393	5.919	2.401	0.966
Partial charge model	3.463	3.442	5.889	2.437	0.974

\*These distances were derived from the atomic coordinates.

TABLE IIX The experimentally determined and calculated structure of P2<sub>1</sub> KOH

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (K-O) (Å)	<i>d</i> (O-H) (Å)
Space group P2 <sub>1</sub> KOH					
Experimental data					
Ibers (1969)	3.95	4.00	5.73	–	–
Jacobs (1985)	3.957	3.995	5.742	–	–
Simulated structures					
LeSar (1982)	3.801	3.849	6.501	–	0.982
Full charge model	3.889	3.928	5.825	2.722	0.966
Partial charge model	3.909	3.921	6.103	2.750	0.973

unit cell with each potassium atom surrounded by a distorted octahedron of oxygen atoms [103]. Unfortunately limited theoretical data [14, 47] exists for monovalent hydroxides.

It is evident (Table IIU–X) that both models offer acceptable descriptions compared to the experimentally determined parameters for all four structures [102, 104, 105]. The ability of the models to predict hydrogen positions, in particular, is hard to assess because there is either a significant degree of variability in the experimental numbers or they are again not reported.

#### 4. Conclusions

Hydroxide containing materials are ubiquitous. Despite this, there have been far fewer modelling studies of hydroxide and oxyhydroxides than equivalent studies of oxides and metals. Nevertheless, there have been a number of excellent previous modelling studies (see for example [14, 15, 47–53, 69, 70, 82]) so that the ability of modelling to contribute to our understanding of such materials is proven.

Part of the reason for the paucity of previous modelling work is certainly the complexity and sometimes uncertainly associated with the experimental structural information in these systems. This is clearly a consequence of how these materials form (often via low temperature processes) leading to poorly crystalline products. From the modelling point of view this makes it challenging to set-up the computations. Of course, it also provides wonderful opportunities to develop new techniques.

Here we have reported two new internally consistent potential models that can be used to model hydroxide and oxyhydroxide systems. Of course, we do not claim that models will be successful for all the associated systems. Pair potentials are limited in their applicability. They do, however, have the advantage of being able to model large numbers of ions. Consequently this study provides a framework for further computational and structural studies. As such we hope that the data contained will encourage others to apply this model and develop new models for hydroxide containing systems.

#### Acknowledgements

Prof. Karen Scrivener of EPFL is thanked for useful discussions.

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