4 Discussion and Conclusion

It has previously been demonstrated that transition metal complex exchanged clays may be generated by contacting the clay with a solution of the choosen complex(23,24). The clays with was choosen to study in this case must have important property called sorption property e.g. laponite, montmorillonite and hectorite. In this experiment, the synthesis of complexes on clay *in situ* was carried out by allowing a transition metal ion exchanged clay to contact a solution of the appropriate ligand. The clay was "bentonite" which is a type of clay in montmorillonite group. In this work the attention was paid to Ni^{2+} and Co^{2+} exchanged bentonite.

This experiment has two main parts.

1. Quaitative study of the effect of ligands on nickel and cobalt-bentonite.
2. Interaction of typical groundwater ligands with nickel and cobalt-bentonite/1M were studied in the context of acidic-basic ligand, metal releasing into solution and the effect of concentration of ligand on complex formation. This clay sample were experimented in 3 steps.
    2.1 Nickel and cobalt-bentonite/1M treated with 3 ligands, ammonia(NH_3), 1,2-diaminoethane(en) and butanoic acid(BA) at equal concentration.
    2.2 Nickel-bentonite/1M treated with NH_3 and BA at various concentration and cobalt-bentonite/1M treated with en and BA.
    2.3 Effect of inorganic salts on the release of nickel ion into solution.

Treatment of Ni-bentonite with NH_3 at various ratio of metal/ligand (1:3, 1:1 and 1:25) when the amount of NH_3 used was more than that of metal ion, there was a characteristic spectral band of $[Ni(NH_3)_6]^{2+}$(11) at ≈572 nm and ≈362 nm in solution. In the case that Ni-bentonite/1M reacted with NH_3

(10.6:1, 1:3, 5:1 and 50:1) it was found that when the the amount of NH_3 was less than that of nickel ion, the spectrum showed a characteristic band of $[Ni(H_2O)_6]^{2+}$(14) at ≈341 nm in solution. When Ni-bentonite and Ni-bentonite/1M clays interacted with this ligand at a ratio of metal/ligand 1:3, complexes $[Ni(NH_3)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$ were formed respectively in solution. It is possible that $[Ni(H_2O)_6]^{2+}$ was formed from $[Ni(NH_3)_6]^{2+}$ by losing NH_3. For the reaction at metal/ligand ratio 1:3, 5:1 and 50:1, the solution spectrum band at ≈295 nm indicating the existance of $NiCl_4^{2-}$(12) in solution. However, when the clay surfaces was analyzed by using UV-vis diffuse reflectance spectroscopy it was found that $[Ni(NH_3)_6]^{2+}$(17) at 530 nm(M:L 10.6:1) or $[Ni(H_2O)_6]^{2+}$ (M:L 1:3, 1:10, 1:25, 5:1 and 50:1) at 700 nm was present

No complexes were formed in solution when Ni-bentonite reacted with en at metal/ligand ratio 1:1 and 1:9, but when Ni-bentonite/1M was used, a characteristic band of $[Ni(en)_3]^{2+}$(16) at ≈235 nm was occured in solution. It can be concluded that formation of $[Ni(en)_3]^{2+}$ will depend on the amount of nickel to be enough to form complex

The addition of DMG to Ni-bentonite showed a characteristic band of $[Ni(DMG)_2]^{2+}$(15) at 540 nm on clay surface. In solution , there was no evidence to show the presence of this complex because this complex was insoluble in water(soluble in alcohol). When this complex was filtered, it moved to sorp on the clay surface.

Nickel clay treated with bipy showed bands at 232 nm and 297 nm which were assigned as bipy bands(14) . There was no evidence of complex formed on clay.

It can be concluded that NH_3, DMG and bipy readily afforded complex of nickel. Ligand en was less efficient than other ligands. However, when en contacted with more concentrated solution of metal, complex of en was formed.

In the case of Co-bentonite treated with at various ratio of metal/ligand (1:3, 1:10 and 1:25) when the amount of NH_3 was more than that of metal ion, there was a characteristic bands of $[Co(NH_3)_6]^{3+(14)}$ at ≈478 nm and ≈352 nm in solution. In the study the reaction of Co-bentonite/1M with NH_3 at 13.1:1 ratio when the amount of NH_3 was less than that of cobalt ion, the spectrum also showed a characteristic band of $[Co(NH_3)_6]^{3+}$ at 491 nm and 350 nm in solution. However, when this complex was analyzed on clay surface it was found that the appearance of $[Co(NH_3)_6]^{3+}$ depended on the amount of metal ion on the clay surface, viz $[Co(NH_3)_6]^{3+}$ was produced on Co-bentonite/1M but not on Co-bentonite.

When the reactions of en to Co-bentonite and Co-bentonite/1M were studied at various metal/ligand ratio the spectral band at ≈467 nm and ≈350 nm of $Coen_3^{3+}$ was found. Only the reaction at 1:9 ratio did not produce the complex of $Coen_3^{3+}$. On the clay surface, a characteristic band of $Coen_3^{3+}$ at 1:1 ratio and 13.1:1 ratio was found. At 1:9, 1:3, 5:1 and 50:1 ratio, this complex was not formed. Thus, it can be seen that the formation of $Coen_3^{3+}$ complex on clay surface did not depend on the metal/ligand ratio.

Investigation of reaction of DMG and bipy with Co-bentonite showed that DMG was a poor ligand and bipy was a good ligand for cobalt ion. The result of bipy in solution had band similar to bipy treated with nickel at 232 nm and 279 nm.

The reaction of cobalt ion with 4 ligands i.e. NH_3, en, DMG and bipy showed that ligands NH_3, en and bipy readily afforded complexes of cobalt ion.

Investigation the influence of acidic-basic ligand on nickel and cobalt/1M, showed that BA(acidic ligand) was a poor ligand for these metal ion in solution and on clay surface. Since BA used oxygen (dornor atom) to coordinate with metal ions, the bond would not be very strong. However, BA released more metal ion into solution than en and NH_3 (basic ligand), supporting the work of Davison and McWhinnie(14). It can be explained that the formular structure of BA is $CH_3CH_2CH_2COO^-H^+$. Which contained $CH_3CH_2CH_2COO^-$ and H^+. H^+ could replace the position of metal ion on the clay surface, releasing them into solution.

Finally, in the study of lability of nickel ion on bentonite, it can be concluded that Ni ion was much more strongly sorbed than Na^+, Ca^{2+} and Cu^{2+}. However, Ca^{2+} and Cu^{2+} were more effective than Na^+ at releasing nickel from clay.

Infrared spectroscopy was used to study the metal complexes of nickel and cobalt clay sample. However it has been found that IR spectral of the metal complexes on clay surface have weak bands because there is little complexes on clay surface and they were shielded by bands of bentonite clay. Thus IR spectral was not used to characterise.