# Abstract

The purpose of hydraulic clayey barriers is to isolate waste liquids from the environment. Bentonite clay is widely used in hydraulic barriers because of its elevated sealing capacity in presence of water. However, exposure to high concentrations of inorganic solutions can change the clay fabric increasing its hydraulic conductivity, with a consequent enormous harm to the environment.

The main purpose of this research was to develop a superior clay with enhanced Hydraulic Performance. An engineered clay (HYPER clay) was developed through treatment of a natural bentonite with an anionic polymer. Furthermore, two commercially available polymer treated clays were studied: a Multiswellable Bentonite (MSB) and a Dense Prehydrated GCL (DPH GCL). To demonstrate the potential benefits of polymer treatment material characterization and swelling tests were performed. Subsequently, hydraulic and chemico-osmotic tests were executed on treated and untreated clays to evaluate the modified clays resistance to chemical attack. Finally a theoretical interpretation of the experimental results was conducted with a newly developed multi-ion system approach.

All experimental and theoretical conclusions of this PhD thesis can be summarized as follows.

The effect of polymers adsorption on clays was studied by physical and chemical analysis that demonstrated the potential benefits of polymers on the sealing, hydraulic and membrane properties of clays. Physical and chemical characterization results proved that the polymer intercalates in the interlayer region of the bentonite inducing a dispersed clay structure and increases the water adsorption capacity of the clay in electrolyte solutions with a consequent potential benefit on the hydraulic performance.

The swelling ability of the treated clays was quantified by means of standard swell index test and swelling pressure tests. Both showed that the treatment with the anionic polymer studied here improved the swelling ability of the untreated clay. The swelling pressure test, compared to the standard swell index test, showed more efficiently the swelling ability of polymer treated clays. Swelling pressure increased also with increasing polymer dosage up to an optimum value.

Hydraulic conductivity tests were conducted on untreated and polymer treated clays. As expected, the hydraulic conductivity of untreated clays increased by permeating the samples with electrolyte solutions due to the compression of the double layer thickness. Conversely, polymer treatment maintained low hydraulic conductivity of the clays to $CaCl_2$ and to sea water in the long term.

The prehydration with addition of polymers and the densification of the commercial product (DPH GCL) preserved low hydraulic conductivities even in presence of aggressive electrolyte solutions such as $CaCl_2$ solutions and sea water.

The low permeability protracted in the long term observed in the polymer treated clays suggested that also the chemico-osmotic efficiency could be maintained with time in presence of aggressive solutions. For this reason, chemico-osmotic efficiency tests were also carried out.

The effect of partial or complete destruction of chemico-osmotic behavior due to diffusion was observed in untreated clays. The clay showed in fact initial membrane behavior, that gradually decreased due to the gradual compression of the double layer thickness due to diffusion of invading cations.

On the other hand, the polymer treatment with the anionic polymer protected the clay against the destructive role of diffusion, maintaining the initial osmotic efficiency in the long term. The polymer treatment modified the bentonite structure such that the double layer thickness of the clay resisted collapse and the membrane efficiency was sustained.

The Swell Pressure and Chemico-osmotic tests results were interpreted theoretically in a newly developed multi-ion system approach. The theoretical development presented here was based on the model proposed by Dominijanni (2005) for 2-ion systems. We developed, in cooperation with the Politecnico di Torino, an extension of the model to allow for multi-ion systems.

With this extension we back analized all experimental data of swelling pressure and chemico-osmotic tests conducted on untreated and polymer treated clays.

We have calculated the swelling pressure of bentonites for 3-ion systems based on the Donnan model and the electroneutrality conditions. We assumed that the number of platelets per aggregate were constant independently of the ion concentration and valence.

We were able to compare the effect of polymer addition and densification based on the back analysis of the swelling pressure tests. Interpreting the experimental data with the model, we demonstrated in fact that the polymer treatment increased the net negative charge of the clay ($C_{X0}$) and limited the aggregation between clay platelets with a consequent improvement of the swelling ability of the clay. Also the densification of a clay increased its swelling pressure. For this reasons, the simultaneous effect of polymer treatment and densification improved considerably the swelling ability of the clay.

For the analysis of the chemico-osmotic tests results we develop an extention of the general model proposed by Dominijanni (2005). In cooperation with Politecnico di Torino, we solved the transport equations for a 3-ion systems in order to interpret correctly the actual multi-ion scenario expected in the site.

The interpretation of the results based on the new model were performed. A parametric study was intended to analyze the impact of the fixed charge concentration of the clay and the impact of the number of clay particles per aggregate on the chemico-osmotic efficiency coefficient vs. time. Whereas, the back analysis of the experimental data allowed to define the fixed charge concentration for both the untreated and polymer treated clays.

The fixed charge concentration of the HYPER clay was higher $C_{X0}$ than that of the untreated clay, whereas, the number of platelets per aggregate was lower. This theoretical interpretation suggests that not only the anionic polymer maintains the interlayer open but also it increases the negative charge concentration of the clay.