FLUORINATED GEOMEMBRANE FOR HYDROCARBON SITE

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Abstract: This paper describes two processes of fluorinating geomembrane for application to a composite cap lining system to rehabilitate a hydrocarbon contaminated site. One process of fluorination was successful while the other process resulted in significant damage to the geomembrane. The paper describes the successful process in detail, and details the lessons learned to achieve an effective fluorinated geomembrane. The fluorination process builds on experience of plastic hydrocarbon storage containers, and expands that knowledge into the geomembrane lining technology. A fluorinated geomembrane provides a higher resistance to diffusion of hydrocarbons through the geomembrane and also improves the durability of the geomembrane in contact with hydrocarbons. The paper also describes the construction part of the works with the associated installation considerations and experience gained with the geomembrane.

Keywords: Fluorinated, polyethylene, geomembrane, volatile organic chemicals, geosynthetic clay liner.

INTRODUCTION

High Density Polyethylene (HDPE) geomembranes (geomembrane) and Geosynthetic Clay Liners (GCL) are extensively used as liner components of environmental containment systems such as landfills, tailings dams, leachate storage ponds, evaporation dams and secondary containment systems for chemical tanks. In these applications GCL and HDPE geomembranes are often used in conjunction to form a composite lining system. For base treatment the geomembrane and GCL liner are used to form a low permeability layer to minimise the migration of contaminants into surface or groundwater. For cap liners the primary function of a composite liner is to minimise rainfall infiltration into the waste and the subsequent generation of leachate. Secondary functions of a GCL and geomembrane in cap lining systems are to reduce gas migration; and to provide containment of leachate weeps from perched leachate.

Historically a strategy adopted for the management of contaminated sites involved the removal of contaminated soil and disposal to landfill, either with or without treatment. In response to increasing pressure to reduce waste going to landfill there is a trend to manage contaminated soil at the source site, through environmental containment of impacted soils which may include capping the impacted soils using either mineral or geosynthetic lining systems.

Environmental containment systems used for the storage of contaminated soil are typically structures similar to landfills and the same basic design principals can be applied. For capping systems of contaminated sites the functions of the cap are the same as those for a landfill cap. However, many of these sites are remediated for the purposes of enabling redeveloping of the site for public use. For such sites, the capping system also needs to provide a physical barrier and separator layer between the contaminated soil and the user of the site. The capping system may also function as a vapour diffusion barrier or attenuation layer where volatile organic chemicals are present in the soil or groundwater.

This paper describes the application of a Fluorinated HDPE geomembrane to rehabilitate a site by capping a former quarry containing hydrocarbon wastes and other organic contaminants. The two processes used to fluorinate the geomembranes are described with discussion of the benefits and issues of the different processes used.

BACKGROUND

The site described in this paper comprised a former basalt quarry approximately 1.5 hectares in size, which was used for uncontrolled disposal of refinery wastes (hydrocarbon sludge and derivatives from refinery process) and other more general municipal waste over many years. In the latter years the materials in the quarry was covered with soil to the crest level of the pit. The filled quarry included an area of hydrocarbon sludge that remained exposed at the surface against one side of the pit. The site was fenced and remained in this condition for many years.

Environmental investigations at the site concluded that surface water infiltration was occurring through the cover soils, resulting in leachate levels in the waste above the surrounding groundwater elevation. This resulted in the migration of leachate mixed with hydrocarbon contaminants migrating offsite.

It was also considered necessary to control the ongoing migration of hydrocarbon vapours off site, to enable the development of the area. To reduce the offsite migration of seepage and vapours it was decided to cap the site with a composite liner and a vapour collection system to enable treatment of the vapours. The after-use of the capped site was to be a public car park.

CAPPING SYSTEM CONCEPT

The exposed sludge was identified as a potential health risk to third parties entering the site, so it was decided to place a temporary soil cover over the sludge area. The cover soil was placed over a woven geotextile reinforcement layer. The mass of the layer of cover soil generated a number of small seeps of hydrocarbon sludge around the area that was covered, which indicated that the waste mass was behaving as a viscous material, and that load placed on the surface is likely to result in surface seeps of leachate and light-fraction hydrocarbons. Testing of the surface seeps indicated that it included hydrocarbon based solvents.

Based on these results, a testing program was undertaken where samples of geosynthetics, comprising High Density Polyethylene (HDPE), polypropylene and polyester were immersed at a temperature of 40ºC to samples of leachate recovered at depth from monitoring wells at the site. These geosynthetics samples degraded severely after 90 days, suggesting that the capping would need additional measures to ensure the durability of the capping system.

On this basis the capping system developed for the site included the following:

- The temporarily cover near surface sludge area was bridged with a reinforced soil mattress comprising stainless steel mesh and clayey gravel fill.
- Leachate and vapour removal system constructed over the surface of the waste. This system included high void ratio materials and trenches to allow the potential pressure dissipation of leachate or hydrocarbon that may result from the capping load.
- GCL as the bottom component of the composite liner of the cap, and to provide a separation layer between potential liquids in the underlying leachate and vapour removal system and the geomembrane over the GCL.
- Fluorinated HDPE geomembrane liner to form the top component of the composite liner.
- Cushion geotextile to protect the geomembrane from traffic loads resulting from the placement of overlying subsoil drainage system.

Over part of the site, the subsoil drainage layer was covered by a crushed rock pavement layer with asphalt surfacing, and over the remainder of the site the liner system was covered with a subsoil layer and topsoil.

FLUORINATED HDPE GEOMEMBRANE

Geomembrane used as part of a composite liner system is well established as an effective barrier to advective migration of organic and inorganic chemicals, and diffusive migration for inorganic chemicals. However, the performance of HDPE geomembrane liners against the diffusive migration of volatile organic chemicals (VOCs) is less effective.

Since the chemical structure of certain solvents (non-polar solvents) is similar to HDPE geomembranes, the solvent and the geomembrane are chemically similar, i.e., the solvent permeates the liner thickness via surface wetting, solvent dissolution and diffusion. Because of the paraffinic structure of HDPE, hydrocarbons and particularly aromatic compounds can permeate and diffuse through its structure.

The effect of surface fluorination on diffusion through high density polyethylene storage containers of hydrocarbon has been investigated primarily by the manufactures of fluorinated products. Diffusion properties of Fluorinated High Density Polyethylene (FHDPE) geomembranes has been investigated in the USA by some manufacturers, but the results are understood to be propriety information and have not been published, as far as the authors of this paper can establish. Research by Sangram and Rowe (2005) related to VOCs migration through FHDPE, and anecdotal information from the manufacturers of fluorinated storage products provided useful information for the development of the design of this project.

The durability of HDPE geomembranes is related to the time it takes for the antioxidants and stabilizers to be depleted. The main factors affecting the loss of antioxidants and stabilizers through the surface of the geomembrane are: the diffusivity of the antioxidants/stabilizers in the HDPE, and increased molecular mobility of the chemicals that results from swelling occurring in response to sorption. HDPE geomembrane exposed to certain liquid hydrocarbon or vapour exhibit swelling. The effect of swelling of the geomembrane is that there is more molecular space for the migration of hydrocarbon through the geomembrane, and the migration or loss of antioxidants from the geomembrane. The hydrocarbon compounds also exert an extractive effect which causes the antioxidants/stabilizers to partition preferentially towards the hydrocarbon phase.

The rate of antioxidant depletion of conventional HDPE geomembrane has been researched over numerous years by various researchers, such as Hsuan and Koerner (1998) among others. One of the parameter used to assess the durability of geomembrane is the Oxidation Induction Time (OIT). The OIT of a geomembrane is reduced when the geomembrane is exposed to hydrocarbon fuels, as investigated by Rimal et al (2004). The same investigation also indicated that the OIT for FHDPE geomembrane exposed to hydrocarbon fuel was up to 2.6 times better than that of HDPE geomembrane.

FLUORINATION PROCESS AND EFFECTS

The manufacture of fluorinated geomembrane can be undertaken primarily in three ways:

- Extrusion of geomembrane with fluorinated resin; or
- Co-extrusion of a fluorinated resin and untreated polyethylene resin; or
- Post-manufacture surface fluorination.

Based on available equipment and timing issues, the fluorination process adopted for this project was post-manufacture surface fluorination.

The process of fluorinating polyethylene was developed over 20 years ago by Air Products in the USA to reduce the permeability of HDPE automotive petrol tanks. More recently fluorination of HDPE was applied to blow-moulded storage containers for chemicals, as the fluorinated HDPE containers were more cost effective than multilayer co-extrusion containers.

By using a mixture of fluorine in nitrogen and oxygen, the fluorination causes a chemical modification of the surface of the polyolefin, thereby enhancing the solvent barrier properties of many polyolefins such as HDPE.

The fluorination benefit is based on the formation of a fluorocarbon barrier layer on the polymer surface, by the replacement of hydrogen atoms on the carbon chains with fluorine. The fluorocarbon barrier changes the surface characteristics of the polymer in terms of polarity, cohesive energy density and surface tension. This in turn has a major effect in reducing the wetting, dissolution and diffusion of non-polar solvents relative to the polymer. Thus fluorination is effective in reducing the permeability of non-polar compounds, including solvents through a polymer surface.

Post manufacture surface fluorination modifies only those polymer molecules near the surface, so there is no significant change to the bulk properties of the geomembrane such as tensile strength and elongation (Rimal et al (2004)). The depth of surface fluorination is related to the time exposed to the fluorination process, which is a function of the diffusion rate of the gaseous reactants of the process.

FLUORINATION PROCESSES ADOPTED FOR THE PROJECT

The process developed by Golder Associates and Fluoroseal involves treating the HDPE geomembrane in roll form. To enable the gaseous reactants to have full contact with the geomembrane surface, two strategies were trialled:

- Embossed geomembrane –The geomembrane trialled comprised spikes on one side of the geomembrane sheet. The spikes kept the adjacent surfaces of the geomembrane in the rolls apart and create a pathway for gas flow through the space to react with the surface of the geomembrane.
- Smooth geomembrane rolled up with geonet – A geonet was incorporated within the roll of smooth geomembrane to create a pathway for gas flow through the geonet and react with the surface of the geomembrane.

It is understood that post-manufacturer fluorination of geomembranes has previously been undertaken by others by the incorporation of a geonet within the geomembrane roll to promote flow of the fluorine gas throughout the roll. It is believed that this project was the first time embossed geomembrane has been used for the purpose of fluorination treatment of a geomembrane.

The embossed geomembrane used was the AGRU (Austria) GmbH "Structure Spike" HDPE geomembrane (Resin Density 0.94 g/cm³). This product has 5 mm high spikes at 25 mm centres on the surface (Figure 1). These spikes kept the adjacent surfaces of the geomembrane in the rolls apart and create an effective flow pathway for gas flow through the space to react with the surface of the geomembrane (Figure 2).

Figure 1. Embossed geomembrane (AGRU Structure Spike)

Figure 2. Embossed geomembrane roll in profile showing space created by spikes

The smooth geomembrane used for the second trail was the GSE Lining Technology (Asia/Pacific) Ltd "HDS 150" HDPE geomembrane (Resin Density 0,94 g/cm^3). The geonet incorporated with the smooth geomembrane was the Geofabrics Australasia Pty Ltd "Geonet" manufactured from recycled HDPE (Resin density 0.80 g/cm^3) with no geotextile component. This type of geonet has a thickness of approximately 5 mm. (Figure 3).

The embossed geomembrane was treated in the 'as received' condition from the AGRU factory with no alteration of the roll for treatment being required.

The combined smooth geomembrane and geonet rolls were prepared, post manufacture, by a geomembrane installation contractor. Rolls of smooth geomembrane were unrolled and then rerolled by hand with the geonet incorporated. The diameter of the roll was limited to 600 mm to maximise the number of rolls that could be treated in a single treatment batch. The contractor was made aware of the requirement to minimise the inclusion of any foreign particles in the re-rolling process, due to the exothermic reaction of the fluorination process.

The fluorine treatment process creates a highly oxidative environment. Particles of materials that are reactive in strong oxidising environments such as organic matter or moisture can potentially cause combustion of the geomembrane during treatment. Significant care was taken during the incorporation of the geonet to minimise the presence of foreign particles. However, during the treatment process several rolls of the combined smooth geomembrane and geonet were damaged by combustion during treatment (Figure 4).

The resultant damage to the rolls was generally focused around specific centres of combustion associated with the presence of an isolated foreign particle that aggressively oxidised on exposure to the fluorine gas causing combustion of geomembrane in the vicinity of the foreign particle.

Geomembrane rolls adjacent to rolls identified as the source of the combustion (Figure 4) were also damaged. Often several layers or more of the geomembrane were damaged in the area of the combustion, with potential thermal altering of several layers of the geomembrane roll near the combustion zone being indicated by discolouring of the geomembrane surface.

Approximately 15 % of the geonet process geomembrane rolls were damaged to some degree by combustion and were rejected from the capping project.

Figure 3. Smooth geomembrane with geonet roll

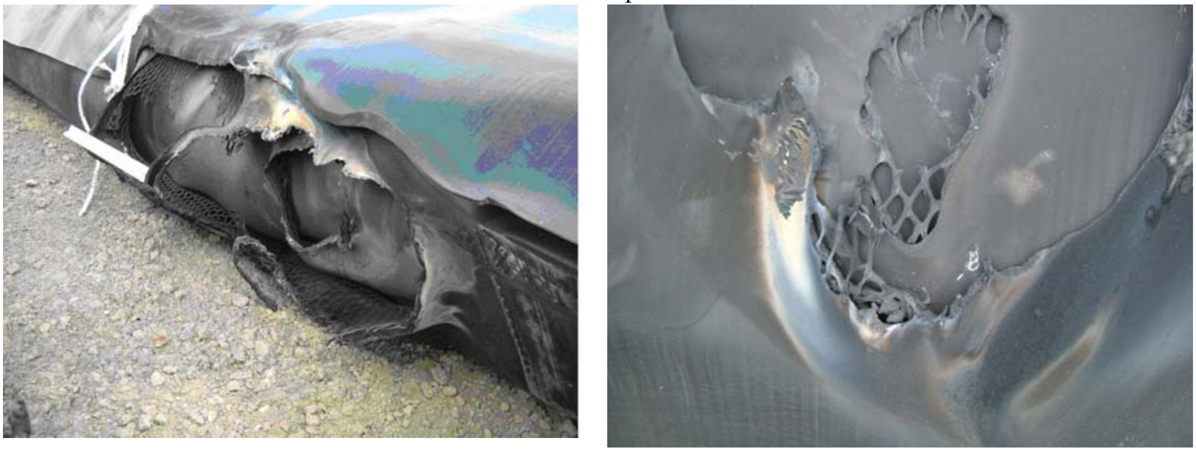

Figure 4. Combustion damaged geomembranes

A review of process for the smooth geomembrane and geonet combination revealed a number of issues:

- The process of rolling up the combined geonet and geomembrane resulted in a “loose” roll with variable gaps between the layers and a relatively more deformable roll. During lifting and placing in the reaction chamber the rolls spooled outwards. This made the rolls difficult to manage during handling for the fluorination process resulting in a variable void space between the wraps in the roll. Mechanised re-rolling would likely improve roll tension resulting in greater uniformity of void space between the adjacent geomembrane surfaces.

- The quantity of geomembrane that can be treated in a treatment batch is dependant on the geomembrane roll size relative to the capacity of the autoclave. It was found that due to low roll tension, fewer smooth geomembrane/geonet rolls could be treated in a batch relative to embossed geomembrane rolls, reducing the treatment efficiency.

Trials indicated that the spike contact area was fluorinated by the diffusion of the gas into the contact area, resulting in 100% surface treatment coverage of the geomembrane surface. Similar effective surface treatment coverage was observed for the smooth geomembrane and geonet rolls although it is believed that the variability in the space between adjacent geomembrane surfaces on the roll could potentially inhibit gas movement across the geomembrane surface.

Fluoroseal indicated that it used 3 times the normal concentration of fluorine gas for HDPE geomembranes as opposed to blow moulded drums and containers. This is partially a function of achieving effective fluorination over the entire surface area of the geomembrane roll.

The concentration of fluorine gas for treatment of the smooth geomembrane with geonet was found to be 1.5 to 2 times greater than the concentration required to treat the embossed geomembrane. This is considered to be probably due to the increase in HDPE surface area created by the inclusion of the geonet.

The surface cohesive energy density of fluorinated geomembrane used for this project was measured to increase from 35 dynes (for the untreated geomembrane) into a range of 55 to 80 dyne.

INSTALLATION OF FLUORINATED GEOMEMBRANE

The fluorination of the surface of the geomembrane occurs at a molecular level and the resultant layer of fluorinated polyethylene is very thin (approximately 3 to 5 microns). It was recognised that extra care would be required to minimise the risk of damage to the surface by scratching or abrasion. Construction specification highlighted the requirement that the geomembrane should be carefully handled to prevent damage and that there was no option to re-fluorination of surface damaged areas, due to the safety risk of working with fluorine gas.

Access across the surface of the geomembrane was therefore restricted and the deployment of the geomembrane was limited to pulling the geomembrane over the underlying GCL only. It was recognised that extrusion welds would be most vulnerable to any hydrocarbon effects, due to the use conventional HDPE extrudate. The use of extrusion welds was minimised, and no extrusion welds were permitted on the underside of the geomembrane, where it was important to preserve the fluorinated layer. Any significant damage to the surface of the underside of the geomembrane was required to be removed and a new panel installed and joined by fusion welding.

Both fusion and extrusion welding methodologies were used to join geomembrane panels. The welding parameters used were similar to those used for a non-fluorinated HDPE geomembrane with the fluorination treatment having no perceived impact upon the weldability of the geomembrane. Strength testing undertaken on seams formed using fusion and extrusion welding methods exhibited weld strengths for both peel and shear failure modes similar to a non-fluorinated HDPE geomembrane seams.

CONCLUSIONS

The capping of hydrocarbon wastes with geosynthetic liners required unusual materials to be used to achieve the performance objectives for the capping system. The potential impact of the hydrocarbon contamination on geosynthetics required the development of manufacturing and installation procedures that required the cooperation of the geosynthetics manufacturer and fluorination treatment contractor during the development of the design and specification.

The use of FHDPE geomembrane, in conjunction with a GCL, allowed a difficult contaminated site to be rehabilitated in line with the after-use objectives of the site owner and community stakeholders.

Two different post manufacturing, autoclave based, fluorination processes were trialled. Fluorination of embossed geomembrane was found to be the more successful process with better treatment efficiency and reduced combustion risk due to the reduced potential for foreign particles to be introduced.

Use of a geonet incorporated within the geomembrane roll was found to potentially limit the distribution of the fluorination treatment through the geomembrane roll and significantly increased the risk of combustion damage to the geomembrane occurring due to the increased potential for foreign particles to be introduced. Treatment efficiency was also found to be impacted for combined smooth geomembrane and geonet rolls as the additional surface area of the geonet requires the use of an increased concentration of fluorine gas.

The use of an embossed geomembrane results in a higher interface friction than a smooth geomembrane and in some applications this can lead to other design issues that need to be addressed, such as where preferential movement planes are required next to a geomembrane.

Incorporation of a geonet as part of the geomembrane manufacturing cycle would reduce the risk of combustion of the geomembrane during fluorination treatment by reducing the potential for foreign particles being introduced through better environment controls. The use of mechanised rollers for the incorporation of the geonet would also improve roll tension leading to better treatment efficiency.

Geomembrane rolls should be wrapped at the point of manufacture to prevent entry of foreign particles during transit.

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