

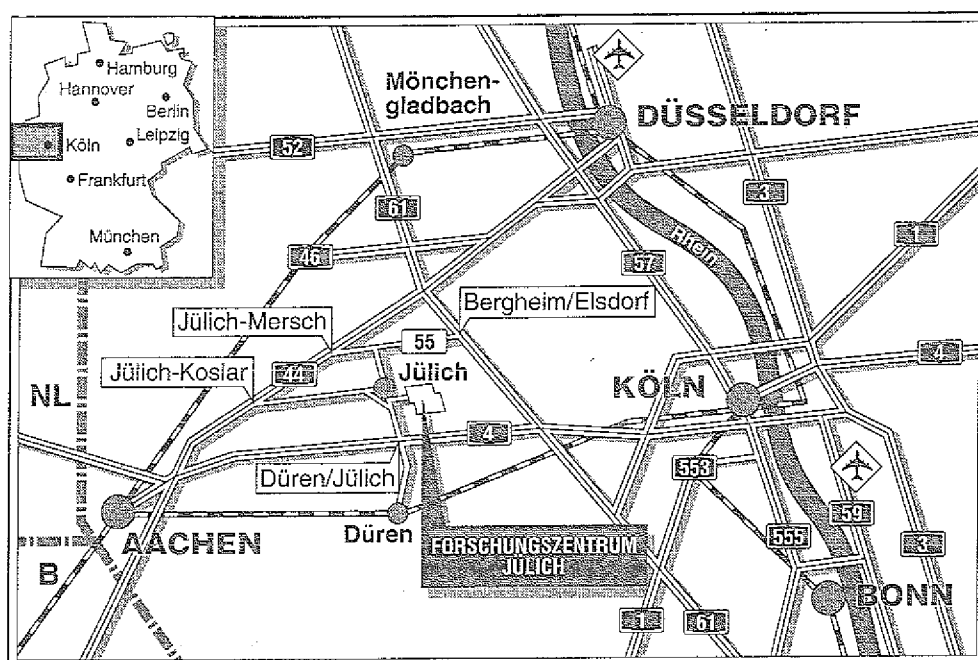
Institut für Chemische Technologie

**Immobilization of MAW in
Alkali-Activated Aluminosilicate
Binders (Geopolymers)**

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M.Y. Khalil* E. Merz

Work performed under Contract No. SR 2004,
Bundesminister für Umwelt, Naturschutz und Reaktorsicherheit

*On leave from Alexandria University, Egypt

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CONTENTS

	Page
ACKNOWLEDGMENTS	3
ABSTRACT	4
1. INTRODUCTION	5
2. BACKGROUND	6
2.1 Solidification of Nuclear Wastes in Aluminosilicate Minerals	6
2.2 Geopolymers	7
3. TROLIT GEOPOLYMER SYSTEMS	9
3.1 TROLIT "AOM"	9
3.2 Investigation of the TROLIT System	11
4. EXPERIMENTAL	17
4.1 Solidification Matrix	17
4.2 Waste Conditioning	28
4.3 Waste Loading and Sample Preparation	28
4.3.1 Waste Loading	28
4.3.2 Sample Preparation	29
4.3.2.1 MAW Samples	29
4.3.2.2 Technetium Samples	30
4.3.2.3 Uranium Samples	30
4.4 Leaching Experiments	30
5. RESULTS and DISCUSSION	34
5.1 Solution Analysis	34
5.2 Sample Behavior in Solution	36
5.3 Results and Discussion	39
6. CONCLUSIONS	50
Appendix A	51
NOMENCLATURE	52
REFERENCES	53

1.1

1.2

1.3

1.4

1.5

1.6

1.7

1.8

1.9

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ABSTRACT

Intermediate-level waste is immobilized in a monolithic solid of low dispersibility. Portland cement, bitumen, and organic polymers are used by many waste conditioning plants to achieve that purpose. However, each has some drawbacks that cause concern, and requires improvements or even the switch to a different better solidifying agent.

Alkali-activated aluminosilicate binders, known as geopolymers, are investigated in this work for possible application in intermediate-level waste solidification. Samples were prepared from commercial geopolymer (TROLIT), loaded with 10 wt.% or 15 wt.%, dry simulated ILW. Quinary brine or water were used as leachants. Samples were soaked for more than six months and the fraction of Sr, Cs, and Mo leached was measured with time. Some samples were loaded with ILW plus NH_4TcO_4 , ILW plus $\text{UO}_2(\text{NO}_3)_2$, or U_3O_8 for comparison. Control samples were made of high alumina cement with sodium-silicate hardener (cement-glass).

Results show that strontium is reasonably immobilized. Its concentrations in water were below detection limit. In Q-brine, 2-7 wt.% was leached in 6 months. Cesium was leached more rapidly than strontium. Leached fractions were 1-11 wt.% and 14-28 wt.% in water and Q-brine, respectively, depending on the composition. Retention of high valence ions, such as Mo^{6+} , Tc^{7+} , and U^{6+} , was poor. 20-40 wt.% of the Mo was leached in water, and 4-18 wt.% was leached in Q-brine. Technetium (starting as NH_4TcO_4) was almost all in the leachant (water or Q-brine) in about one month. From solidified $\text{UO}_2(\text{NO}_3)_2$ plus ILW, 36 wt.% was leached in water. The results for Sr, and Cs are better than those published for ordinary portland cement. However, the values obtained for technetium and uranium are unfavorable.

Tolerance of solidified matrix to water was quite adequate. Samples maintained their shape, dimensions, and strength to the end of the experiments. On the contrary, tolerance of most compositions to Q-brine was poor. Samples were sometimes cracked between one and four weeks. Some compositions experienced no changes through the experimental duration.

In comparison, cement-glass gave better results under the same conditions. Concentrations of Mo, and Sr were below detection levels in all cases. Cs was also not detectable in Q-brine. Only 4-6 wt.% of cesium was leached into water. In addition, tolerance to both water and Q-brine was quite good.

1. INTRODUCTION

Radioactive liquid wastes are generated in most nuclear fuel cycle processes. They are also generated in other industries, hospitals and research facilities. Most of this waste can be classified as low level waste (LLW) or intermediate level waste (ILW)*. According to the IAEA classification two levels of LLW (37 kBq to 37 MBq and 37 MBq to 3.7 GBq, B/g activity/m³) and all the ILW (3.7 GBq to 370 TBq) are required to be treated (1). In most cases solidification and stabilization are necessary prior to final disposal.

Immobilization is accomplished in most cases by incorporating the wastes in a monolithic solid of low dispersibility. Among several inert binders used to immobilize waste liquids, cement, bitumen and organic polymers are the most accepted and used most frequently (2). Nevertheless, each has its advantages and disadvantages.

Hydraulic cements are widely used for the solidification of liquids and sludges. Additives can be used to adjust the properties of cements to accommodate individual waste constituents and improve the solidification process. Cement has the advantages of well-known technology, compatibility with many wastes, good strength, low leachability to some nuclides and low cost. However, some wastes may affect the setting processes, cement requires pretreatment of most wastes, and swelling or cracking with some products under exposure to water.

Bitumen is also used in a number of forms as an immobilizing agent. It has the advantages of well-known technology, no free-standing water, no problem with improper setting, low leachability, and quite low cost. However, bitumen also has the disadvantages of limited loading of salts, may swell in water, flammability, radiolytic gas generation, and interference to heat.

Organic polymers (e.g. polyester-type resins) offer the advantages of being adaptable to many wastes, no free-standing water, high compression and impact strength and relatively low leachability. However, they have some disadvantages such as limited binder shelf-life, some wastes may interact chemically to prevent polymerization, and relatively high cost.

Although these three immobilizing agents are used to different extents in the nuclear industry, none satisfies the optimal requirements of a host phase. Therefore, the door is still open for new host materials that may compete with existing ones.

* Also (MAW) for Medium Activity Waste.

This research work is concerned with the utilization of relatively new materials in the nuclear field, known as "geopolymers" for immobilization of ILW. Geopolymers are aluminosilicate network binders that extend in three dimensions. Two important characteristics attracted attention to geopolymers as a host phase for radwaste. First, the fact that geopolymers set at low temperature (10 - 100°C) to give amorphous to semicrystalline structure. Second, the product material is superior to cement in its chemical properties (very low solubility in all organic and inorganic solvents), mechanical properties, and water contents (less than 1 % when heated to 100°C). However, several properties related to radioactive waste immobilization applications are not known. What is the rate of leaching of geopolymer matrix and hosted waste? How much waste loading is possible without increasing leachability or changing mechanical properties beyond acceptable limits? What are the radiation effects on the properties of geopolymers? And finally how good are geopolymers in retaining some specific elements such as Tc and U? Such questions are addressed in this project.

2. BACKGROUND

2.1 Solidification of Nuclear Wastes in Aluminosilicate Minerals

Fixation of radioactive wastes by hydrothermal reactions with aluminosilicate mineral clays has been extensively studied since the early work on nuclear waste (3). Most of the work was done to incorporate cesium and/or strontium in a definite aluminosilicate mineral. Barney (4) described a low-temperature process for the conversion of radioactive sodium salt wastes into solid sodium aluminosilicates. This was accomplished by the reaction of waste solution with powdered clays such as kaolin, bentonite, holloysite, or dickite to produce small crystals of cancrinite. The reaction takes place between 30°C and 100°C and requires two moles of NaOH per mole of cancrinite formed. Salts, including radioactive ones, are trapped in the cancrinite crystal lattice. The leach rate in distilled water was reported as 10^{-7} to 10^{-9} g of sample/cm² day.

Thompson (5) demonstrated the possibility of solidification of simulated alkaline high level waste solutions by reaction with silica, bentonite and phosphoric acid. The processes were developed only for interim storage of liquid waste. Therefore, the products were not leach-resistant and do not satisfy the general requirements of solidified phases.

Barney (6) synthesized different crystalline aluminosilicate phases containing cesium; pollucite, cesium zeolite, cancrinite and sodalite. Original aluminosilicate reagents were either bentonite, kaolin, pyrophyllite or aluminosilicate gel. He used waste compositions that were either pure CsOH or mixed with NaOH, NaNO₃ or NaCl. The product crystallite sizes were between 0.1 and 4 μm. Their thermal stability was good and leach rates were around 10^{-4} g/cm² day.

Another development was carried out by Thompson (7) in which he mineralized Cs contained in supernatant into sodalite and cancrinite by reacting the alkaline cesium containing waste with kaolinite. He also fixed cesium in zeolite, which showed leaching rates 10^4 times less than those of sodalite and cancrinite. Simulated high level waste (HLW) sludge was solidified, hot mineralized by reaction with NaOH and silica gel to give a hard monolith. Since the sludge contained $\sim 50\%$ $\text{Al}(\text{OH})_3$, the solidified product is more or less similar to the product under consideration in this study.

The goal in all previous studies was always the same; which is to incorporate cesium from alkaline waste solution in a crystalline aluminosilicate mineral. The later is to be further solidified into a monolith using cement or glass. Although, successful products were accomplished, the work was not developed further since the idea of HLW partitioning was abandoned and shortly after that glass and ceramic techniques were developed and accepted.

Davidovits (8) in a quite vague and inconclusive patent proposed that waste can be combined and mixed with alkali-activated silico-aluminate geopolymer binder. The silico-aluminate proposed is a clay of the kaolinitic type. The patent claims a good solidified product for toxic mine tailings, but it does not include radioactive waste of any sort (9, 10).

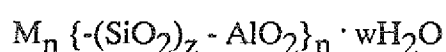
2.2 Geopolymers

The name "geopolymer" was invented by Davidovits (11) to describe a family of mineral polymer binders known since the 1940's (12). It implies that a group of minerals undergo polycondensation and form rapidly at low temperature similar to organic polymers. However, they are inorganic, hard, noninflammable, and stable up to high temperature ($\sim 1200^\circ\text{C}$), similar to mineral materials. The chemistry and properties of geopolymers have been detailed repeatedly in many publications (13-22), and many other patents. The most comprehensive review regarding the development and properties of aluminosilicate binders is presented by Malone (23). A summary of the structure and properties of alkali-activated aluminosilicate binders (geopolymers) is presented here.

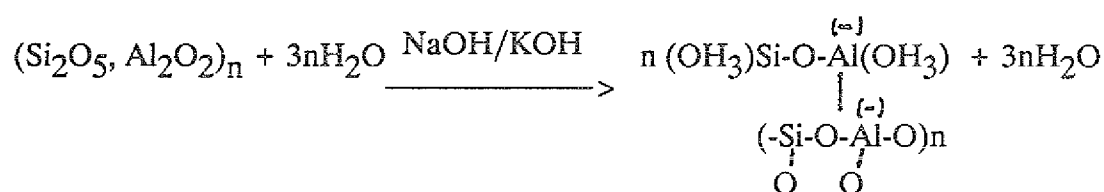
Alkali-activated, aluminosilicate binders are a set of materials that are formed by the reaction of alkali solution with fine grain solid that is rich in silica and alumina. A wide variety of conditions are acceptable in which silica, alumina, and alkali metal existing together in high pH solution will lead to the formation of aluminosilicate binders. Slags, industrial ash and dust, and clays are all potential reactive materials. Silica can be supplied as sodium or potassium silicate. The alkali metal component is supplied as NaOH, KOH, or their soluble salts.

Setting reaction starts with the alkali attack on the amorphous silica with the formation of a sodium-silicate layer on the solid particles. Aluminium oxides dissolve directly in the sodium silicate. A gel of aluminium, silicon, alkaline earth elements, and water is formed. As the gel begins to coalesce, bound water is expelled and the binder becomes relatively fluid. Silicate and aluminium hydrates begin to form zeolite-like products. It is difficult to specify the type of zeolite formed since it depends to a great extent on the composition of the mixture and the conditions of formation. Separate zeolite crystal phases have not been clearly identified in x-ray diffraction studies of alkali-activated binders. Some studies have indicated that mixed sodium-calcium hydrosilicates are formed rather than separate sodium or sodium-calcium alumino-silicates that can be identified as zeolites (23). Despite the reaction pathway, geopolymerization is exothermic.

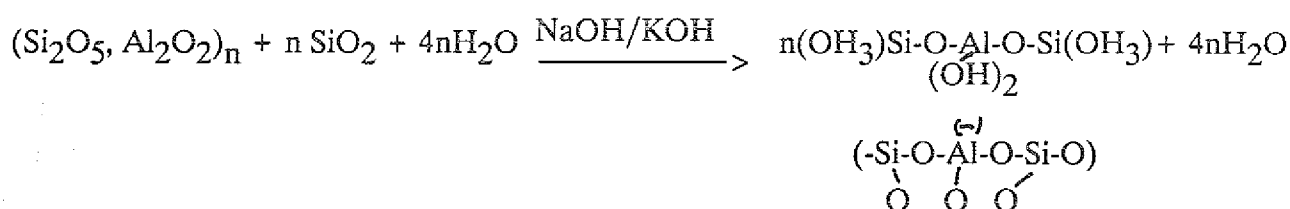
Davidovits (19) suggests that a silicon-oxo-aluminate network is formed consisting of SiO_4 and AlO_4 tetrahedra, linked alternately by sharing all the oxygens. Positive alkali metal ions (Na^+ , K^+ , Li^+), alkaline earth ions (Ca^{++} , Ba^{++}), NH_4^+ or H_3O^+ must be present in the framework cavities to neutralize the negative charge of Al_3^+ in IV-fold coordination. However, this structure of aluminosilicates has been known for quite some time (24). The general formula for such a composition is



where M is a monovalent cation, n is the degree of polycondensation and z is 1, 2 or 3. The final framework structure formed is based on the starting composition. Analcime, sodalite, kalsilite, phillipsite, leucite or other three-dimensional aluminosilicates can be formed. The geopolymerization reactions can be schematized as follows (13).



or



among other possible reactions.

Aluminosilicate binders possess some general characteristics that can be summarized as follows.

- Setting temperature less than 100°C.
- High pH of reaction system; 13 - 14.
- Low shrinkage on dehydration (less than 1 % at 400°C and less than 2 % at 800°C).
- High fusion temperature: 1050 - 1250°C.
- Excellent freeze-thaw durability
- Compressive strength is 20-40 percent higher than type I portland cement after 28 days. An alkali-activated binder is reported to reach over 50 MPa unconfined strength in less than one day.
- Coefficient of linear expansion is $0.9 - 1.3 \cdot 10^{-5}/^{\circ}\text{C}$.
- Excellent chemical stability in organic solvents, alkaline and saline solutions. Good in concentrated H_2SO_4 and poor in concentrated HCl.

3. TROLIT GEOPOLYMER SYSTEMS

TROLIT is the trademark of a set of aluminosilicate binders produced by Hüls Troisdorf AG. TROLIT (AOS), for instance, is used for the production of foam (density $0.3 - 0.8 \text{ g/cm}^3$) with open or closed cells. This can be applied mainly for heat or sound insulation or for fireproof construction components. TROLIT (AOM), on the other hand, is a compact material (density $1.5 - 3.0 \text{ g/cm}^3$). TROLIT (AOM) is the target of this study, hence, a detailed analysis of the system is given here. All technical information and data in this section were obtained from reference (25).

3.1 TROLIT "AOM"

TROLIT is supplied as a separate powder matrix and liquid hardener. The latter is a mixture of sodium and/or potassium-silicate in addition to possibly the hydroxides of these two alkali-metals. The pH value of the hardener is higher than 13, which provides the right conditions for aluminosilicate network formation. The solid part of TROLIT is also two components; reactive material and fillers. The latter is added to increase the volume and improve the properties of the final product. The reactive component reacts with the hardener to form an aluminosilicate network. In fact, TROLIT may contain one of three reactive components, namely, ROS, KOS, or metakaoline. Two proposed recipes for TROLIT are given in Table 1. When also considering the hardener added, the reactive material forms only one quarter of the TROLIT solid matrix by weight.

Material	BHL 93 a g	E 61058 g
Talc/R6	120	120
Al ₂ O ₃ -CALZ	240	120
Zircon sand	200	240
Reactive Material Type ROS	240	140
Reactive Material Type KOS	240	140
Reactive Material Type Kaolin	240	140

Table 1: Proposed recipes (E 61058 and BHL93a) for TROLIT (AOM)

Reactive components ROS and KOS are corundum dusts which are by-products of the aluminum industry. Metakaolin (or kaolin) is a normal china clay. ROS and KOS are fine particles (few μm to one mm) with KOS has finer particles than ROS. Every particle is a core of mainly Al₂O₃ and a shell of mainly SiO₂. The average EDX analyses of ROS, KOS and kaolin are given in Table 2. The XRD analysis of reactive materials ROS and KOS shows only SiO₂ and Al₂O₃ peaks.

Component	ROS	KOS	Kaolin
Al ₂ O ₃	59.1	59.6	43.2
SiO ₂	29.7	34.0	53.1
Fe ₂ O ₃	6.23	3.38	0.9
K ₂ O	0.79	0.6	3.1
TiO ₂	1.7	1.15	-
Ga ₂ O ₃	0.22	-	-
Na ₂ O	0.31	0.48	-
MgO	0.75	0.69	-
Cr ₂ O ₃	0.25	-	-
SO ₃	0.17	-	-
Cl	0.034	-	-

Table 2: Average EDX analysis (weight %) of reactive material; ROS, KOS and kaolin

The most important properties of TROLIT stated by the supplier are as follows.

- Temperature resistance up to 1500°C
- Incombustibility
- Resistance to most solvents, organic and inorganic. However, less resistant to nitric acid and poor resistance to hydrochloric acid.
- High hardness, bending strength, compression strength and Young's modulus of elasticity.
- Good vibration-damping properties.
- Low coefficient of thermal expansion.

Most of these properties are attractive from the waste immobilization application standpoint. However, some other properties specifically related to this application need further investigation.

3.2 Investigation of the TROLIT System

A preliminary study of TROLIT was performed to determine the dimensions of leach experiments. The nominal ratio of hardener to solid is 30 % by weight. At this ratio the mixture is soft and sticky. This always leads to entrapped air bubbles which are difficult to liberate unless mixing takes place under vacuum or vigorous mechanical vibrations are used. Ultrasonic waves did not prove to be adequate.

The mixture usually hardens in almost 20 min. at room temperature and in a few minutes at 80°C. The final density attained for a bulk sample dried at temperatures higher than 100°C is between 2.5 and 2.8 g/cm³.

Some attempts were made to form the material with as little hardener as possible. At 10 % hardener the mixture was dry and cannot be cast by any means. At 12.5 % hardener the mixture could be formed under pressure. A pellet that formed under 40 KN pressure (force) withstood free pressure (force) of 13 KN (cross section area ~ 1 cm²) when dry. At 15 % the mixture hardens in a few minutes at room temperature.

Experiments were also performed to investigate:

1. The leach rate of composition elements mainly Si, Al, Na and K.
2. The effect of cure temperature on the hardness of the final product.
3. The effect of hardener to solid ratio on the hardness of final product.
4. The effect of thermal cycling.
5. The effect of changing the filler ratio.

Details of experimentation procedures and numerical results will not be given here. Instead, summaries of final results and conclusions are presented.

- For leaching experiments, samples with $\sim 3.5 \text{ cm}^3$ volume ($H \sim 2.85 \text{ cm}$ and area $\sim 1.19 \text{ cm}^2$) were made of two different compositions; 15 % and 30 % hardener. These were soaked in Q-brine and DI water at 50°C . Solution samples were taken after 7 days and analyzed for Al, Si and Na contents. Results showed that leaching of Al and Si was higher in water than in Q-brine. Al was 25 to 50 times higher in water than in Q-brine. For Si and Na the leached fraction was higher for 15 % hardener than 30 % hardener. However Al had the opposite effect. It is likely that Al was leached in its hydroxide form, while Si and Na leached out as sodiumsilicate.
- To investigate the effect of curing temperature on hardness as a function of time 44 samples (volume $\sim 3.5 \text{ cm}^3$) were made with 30 % hardener. These were divided into three groups. One group was stored at room temperature, the second at 50°C , and the third at 80°C . Unconfined compression test were performed after 1, 2, 7, 16, 21 and 27 days. Samples stored at 80°C attained their highest strength in one day. Samples stored at 50°C reached the same strength in about one week. However samples stored at room temperature did not achieve the same strength even after 27 days. Figure 1 shows the change in compression strength as a function of time for the three samples.
- The effect of hardener to solid ratio was examined by forming three sets of samples with 15 %, 20 % and 40 % by weight of hardener. These were cured by the standard procedure (one day at 80°C), then stored at room temperature, and unconfined compression tests were performed after 1, 7 and 15 days. Samples with 20 % hardener showed the greatest strength, which indicates that there was enough hardener to complete the reaction and form the aluminosilicate network. Samples with 15 % harder were next in strength. Samples with 40 % hardener showed the lowest strength. This can be explained in terms of excess waterglass, which forms separation zones among networks of aluminosilicates. Figure 2 shows the variation in compression strength for these samples.
- Samples with 30 % hardener were formed by the standard procedure. These were cycled between 0°C and 50°C (12 hours each) and the compression test was performed after 1, 7 and 16 days. The results revealed no noticeable change in strength as a result of thermal cycling: at least within the period of the test.

- The effect of changing the filler ratio was also studied by forming a mixture with 30 % hardener. This was divided into four parts and fine talc powder was added with ratios (to the original solid material) of 10 %, 19 % and 31 %. Samples were dried at 80°C for 24 hours, then a compression test was performed. The results are shown in Figure 3. It appears that adding up to 10 % talc would close the pores and increase hardness. More talc will disturb the structure decreasing the strength rapidly.

The solidification of MAW required more fundamental testing of geopolymers. Therefore, upon our request the Hüls Troisdorf AG supplied the components of TROLIT separately namely: the reactive material (ROS) and three other fillers to increase density and strength. The company also supplied two more active materials (KOS and Kaolin) which can be mixed separately to the same ratio with fillers. After few experiments the reactive material kaolin was excluded since it is expensive and does not solidify easily with waste components. Hence, work concentrated on ROS and KOS as the active materials.

To save time, analysis efforts and costs the attitude of "Solidify and Leach" was not adapted. Instead, very large numbers of experiments were conducted, qualitatively evaluated, and unpromising directions were excluded. The matrix of experiments is multidimensional and difficult to show graphically on a two-dimensional paper. One can imagine its size by considering that all possible combinations of the following parameters were examined:

1. Host Material

- * KOS
- * ROS
- * SECAR 51
- * Waterglass

SECAR 51 and waterglass were also investigated to compare the results with TROLIT.

2. Filler (only for KOS and ROS)

- * No filler.
- * One half the filler recommended by Hüls.
- * The filler recommended by Hüls.

3. Hardener

- * TROLIT hardener
- * PAW (waterglass)
- * PN (another waterglass)
- * FABUTIT 748 (for waterglass only)

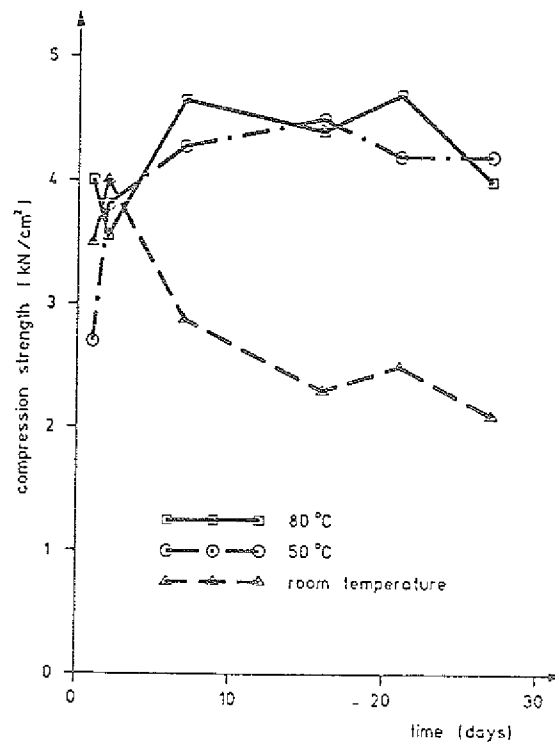


Figure 1: Cure temperature effect for ROS Geopolymer + Filler TROLIT (tradename HÜLS company)

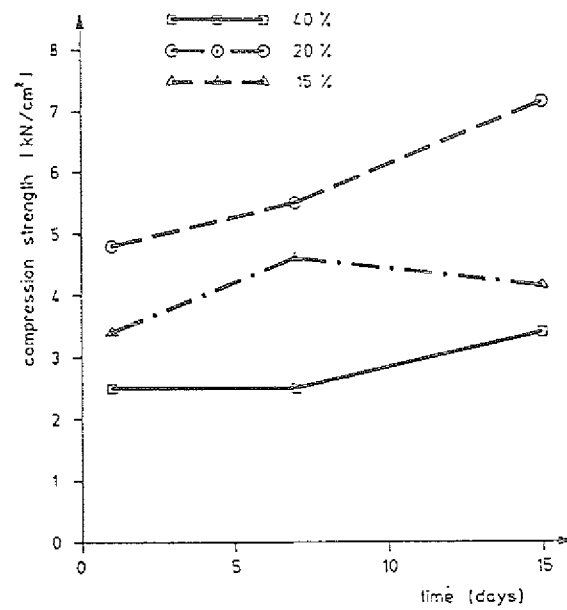


Figure 2: Effect of hardener (KOH) to reactive material (KOS) ratio

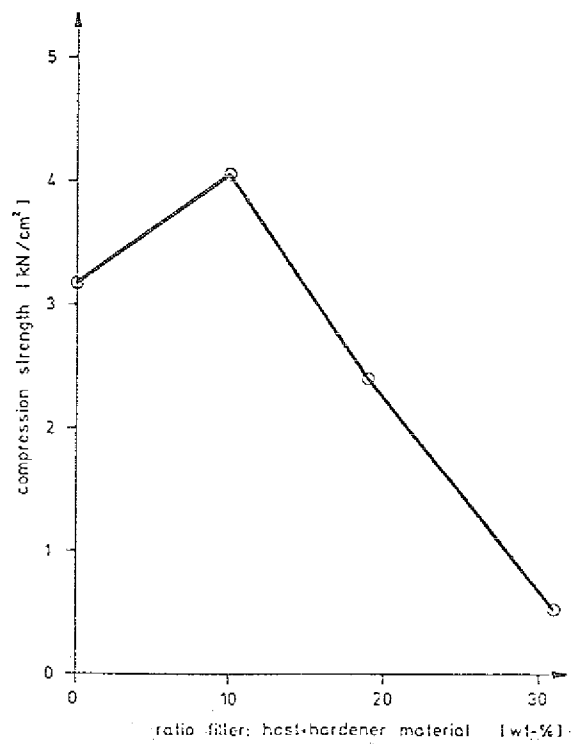


Figure 3: Effect of filler to host material + hardener weight ratio

4. Hardener ratio

- * 20 %, 30 % and 40 % for geopolymer
- * 30 % and 50 % for waterglass.

5. Cure temperature

- * Room temperature
- * Room temperature then 80°C
- * 80°C

where PAW (Portil AW) and PN (Portil N) are two types of waterglass with different Si/Na ratio supplied by Henkel KGaA Düsseldorf. SECAR 51 is a high temperature cement which is mainly alumina-lime and can be hardened by mixing with waterglass supplied by La Farge Tonerdezement. FABUTIT 748 is an aluminum phosphate hardener for waterglass supplied by Chemische Fabrik Budenheim, Rudolf A. Oetker.

These combinations were boiled down to 11 different solidification conditions that are taken to the leaching stage. They are some combinations of the following parameters:

1. Host Material

- * KOS
- * SECAR 51
- * ROS

Although waterglass samples had solidified very well, they cracked on contact with water and were removed from the experiments.

2. Filler

- * The amount of filler recommended by Hüls AG and given in section 3.1.

3. Hardener

- * TROLIT hardener (AOM E61062 for KOS and ROS)
- * PAW (For SECAR 51 and ROS)
- * FABUTIT 748

4. Hardener ratio

- * 20 %, 30 %, 40 % for ROS
- * 30 % for KOS
- * 40 % for waterglass and SECAR 51

5. Cure temperature

* Room temperature then 80°C

As expected, the attempts to solidify iodine-loaded AC 6102 were not successful. The reaction between the highly alkaline hardener and AgI is so strong that some of the samples did not harden. Others were weak and collapsed on contact with water. Such results were apparent from previous knowledge of the instability of AgI in alkaline solutions. Therefore this direction was not pursued further.

4. EXPERIMENTAL

4.1 Solidification Matrix

Geopolymer systems with both KOS and ROS as active components were used. The KOS system has finer grains than the ROS system, which means better reaction and less porous products. Therefore, a few experiments were carried out to examine whether that had any substantial effects on waste immobilization. Table 3 gives the composition of the different matrices.

Sample Code	Reactive Component	Hardener Ratio [wt.-%]	MAW Loading [wt.-%]
GP-1	ROS	30	10
GP-2	ROS	30	15
GP-3	ROS	20	10
GP-4	ROS	40	10
GP-5	ROS	30	10
KP-1	KOS	30	10
KP-2	KOS	40	15
S-1	SECAR 51	40	10
S-2	SECAR 51	40	15

Table 3: Composition and loading of geopolymer systems used for MAW immobilization

The hardener in samples GP-1 through GP-4 and KP-1 and KP-2 is the same, namely a mixture of sodium and potassium silicates supplied by the HÜLS Troisdorf AG as (AOM E61062). In samples GP-5 the hardener (PAW) is only sodium-silicate prepared from powder (PORTIL AW supplied by Henckel AG) with a final percentage weight fraction of 30 %, 15 %, and 55 % for SiO₂, Na₂O, and water, respectively. In all cases, the hardener ratio is expressed as a percentage of the dry solid component of the system which is either ROS or KOS

plus the other additives. Waste loading is not included in this ratio. For comparison, cement of the SECAR 51 type was hardened with 40 % by weight of the PAW preparation. Waste loading in this matrix is 10 % (S-1) or 15 % (S-2) by weight. Cement solidified with sodiumsilicate is called cement-glass by some workers (26-28).

Changing the solid mixture components ratio, additives/ROS or KOS weight, had a strong effect on the final solidified product. The mixture either did not harden properly or gave a weak solid that was easily breakable. Hence, the choice was to bind to the original recipe given in the previous section. The bulk compositions of loaded geopolymer matrices and S-2 are given in Table 4 as measured with EDX.

Composition [wt.-%]							
Element	GP-1	GP-2	GP-3	GP-4	GP-5	KP-2	S-2
Na	5.97	6.51	6.50	5.99	8.01	10.17	9.96
Al	28.42	28.07	34.14	27.83	32.48	17.90	36.59
Si	33.27	35.68	33.11	32.63	41.75	43.86	15.29
K	21.05	11.89	9.77	21.83	1.86	12.90	0.39
Ca	0.70	0.59	1.29	0.67	0.69	1.95	32.93
Ti	0.53	1.42	0.89	0.83	0.66	0.52	1.86
Fe	6.35	9.50	10.43	6.33	9.89	4.24	1.99
Mn	0.86	2.43	1.60	1.18	-	0.30	-
Zr	2.83	2.40	2.53	1.67	4.17	0.00	-
Mg	-	1.50	0.63	1.05	0.48	8.14	0.97
	100	100	100	100	100	100	100

Table 4: EDX bulk composition analyses for loaded geopolymers

Despite the difference in hardener to solid ratios and waste loadings, samples GP-1, GP-2, and GP-4 maintained relatively constant composition of Na, Al, and Si. This is a strong indication that similar or the same matrix structure is formed in each case. The extra components such as sodium from the waste or sodium and silica from excess hardener were either rejected with the reaction water or remain incubated in the matrix. The similarity of the structure appears in the SEM micrograph shown in Fig. 4 and 5 for GP-1 and GP-4, respectively. What is not clearly understood is the low concentration of potassium and high concentration of iron in GP-2 and GP-3. Also, it is not clear whether these two concentrations are interrelated. In general, the SEM examination of samples GP-1, and GP-4 revealed one continuous major phase with a few spots of nonreacting materials that are mainly silicon and potassium (from the hardener), aluminum (from ROS), or zirconium (from the additives). Samples GP-3 had

higher concentrations of nonreacting ROS and samples GP-4 had higher concentrations of free hardener. Again Fig. 4 is an SEM micrograph of GP-1 showing a piece (about 70 micron long) of nonreacting material which is 94 % Al. Also, Fig. 5 is a similar micrograph from GP-4 in which the two large pieces are mainly Al, and the round one at the bottom is Si and K.

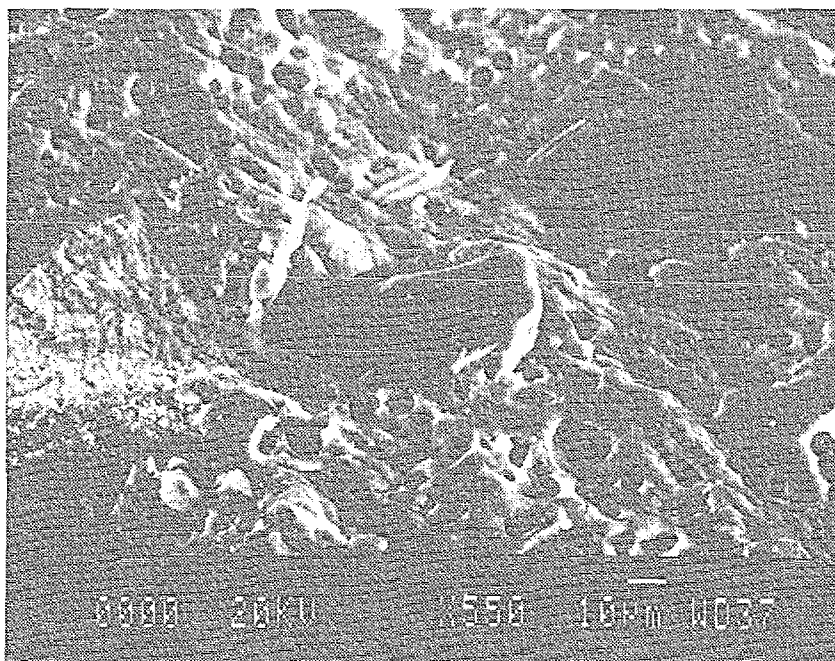


Figure 4: SEM image of sample GP-1

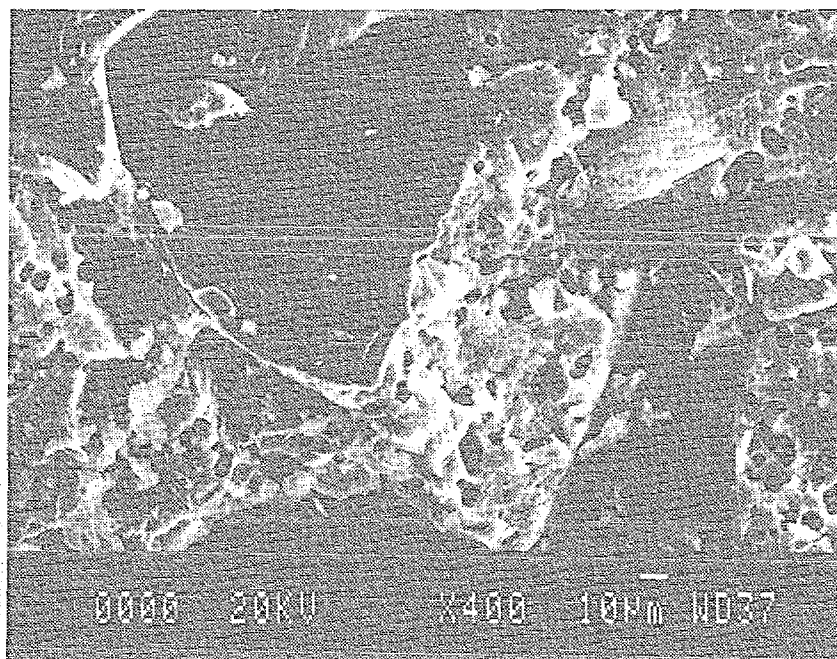


Figure 5: SEM image of sample GP-4

The structures of GP-1, and GP-4 are also similar in containing two categories of pores. Large pores are 5-10 microns as they appear from the micrograph of GP-4 in Fig. 6. Small pores are < 1 micron in diameter. They can be seen in Fig. 7, which is a higher magnification of the large solid area to the right of the center line in Fig. 6. On the one hand the large pores are likely to have formed as trapped air bubbles around which the matrix solidified. On the other hand, small pores are believed to have contained the produced reaction water. As this water was formed while the system was hardening, it was not possible for the pores to grow larger than the submicron size. This water probably gradually evaporated out of the system when the temperature was raised to 80°C as a step in the curing process. Rejected water with some soluble components was then precipitated on the outer surface of the samples as a white layer that will be discussed in the sample preparation section.

The bulk compositions of samples GP-5 (Table 4) are different from GP-(1 and 4). As mentioned earlier, the hardener was only sodium silicate. The percentage of Na and Si in the bulk composition is relatively high. The SEM micrograph in Fig. 8 shows that there is also a difference in the structure of GP-5 as compared to GP-(1 and 4). The GP-5 structure looks like submicron grains cemented together. This is likely to leave a free path to the surface, which can also be concluded from the amount of water and soluble components that escaped and precipitated on the surface. GP-5 had more than twice as much precipitate as GP-1.

GP-2 and GP-3 are closer in their composition to GP-1 and GP-4. However, their structure is very close to that of GP-5. Figs. 9 and 10 show the microstructure of these two compositions. Comparing GP-(1 and 4) and GP-(2, 3, and 5), it is believed that within a range of composition a certain structure will form and outside that range different ones. By comparing the compositions of GP-(1 through 5) there appears to be one main factor that has affected the structure differences; namely, the pH of the medium. Since the waste simulate has quite a low pH value ($\text{pH} = 1$) it could alter the conditions necessary for polymerization. Therefore, it is likely that a waste/hardener ratio > 0.33 might cause the formation of only small grains at localized high pH regions where the conditions are favorable. In sample GP-5 the same results were achieved with waste/hardener ratio of 0.33, due to the relatively lower alkalinity of the PAW hardener ($\text{pH} = 12.3$).

The bulk composition of KP-2 was also different from other GP samples. However, they cannot be compared since the starting reactive component, KOS, is different from the ROS in the GP samples. Nevertheless, one cannot help noticing that the composition contains about double the Na and the almost the same K compared to GP-2 which has the same loading. The structure of KP-1 and KP-2 is more or less similar to the GP-(2, 3 and 5) family judged by the SEM micrograph shown in Fig. 11.



Figure 6: SEM image of large pores in sample GP4

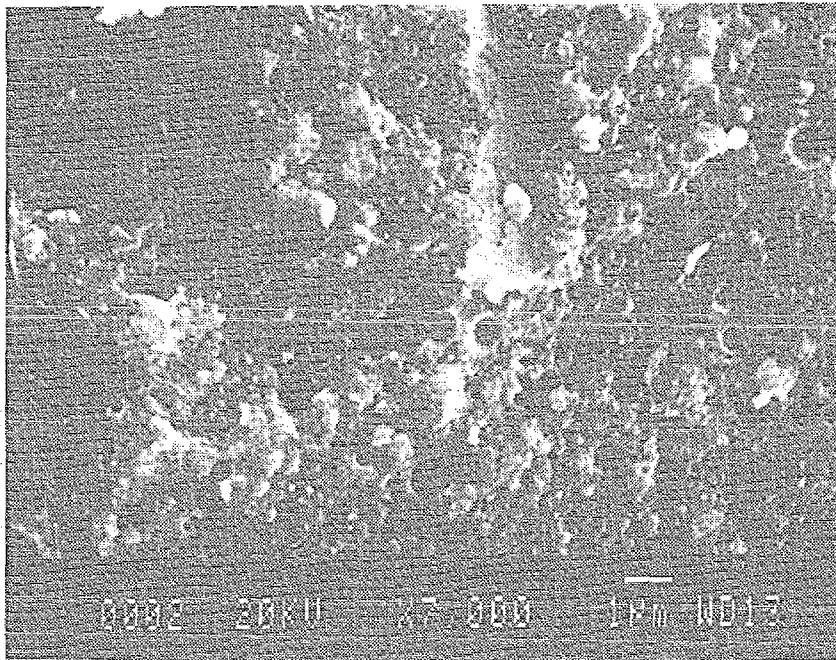


Figure 7: SEM image of small pores in sample GP-4

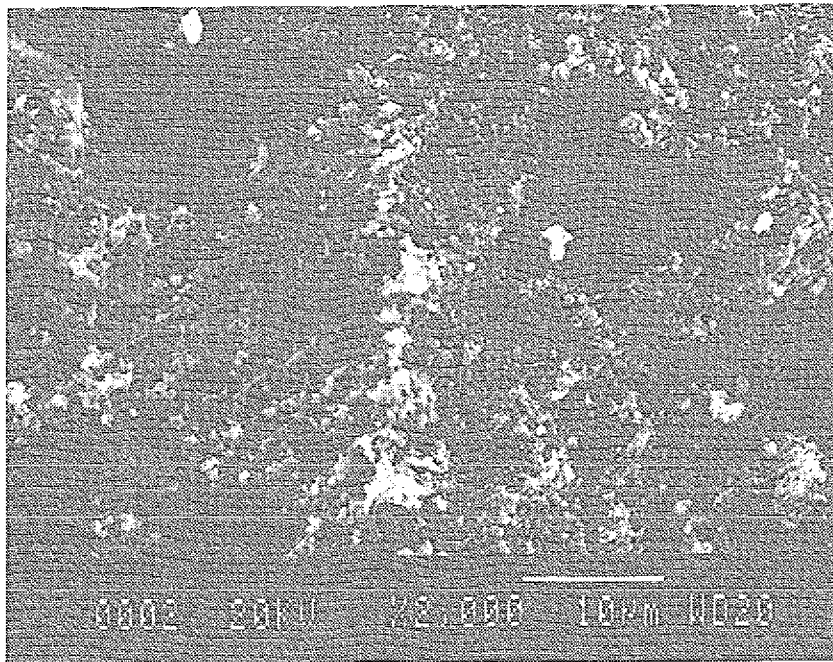


Figure 8: SEM image from sample GP-5

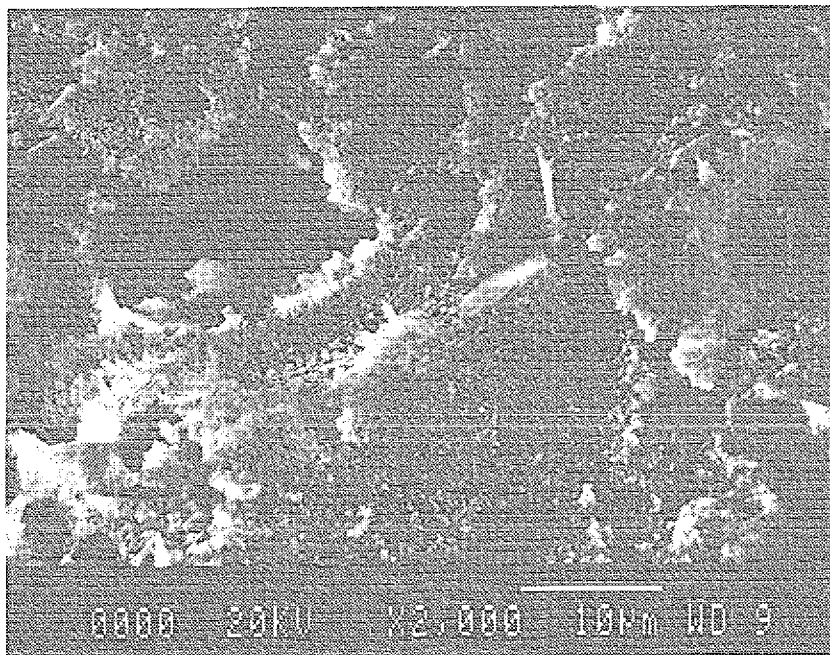


Figure 9: SEM image from sample GP-2

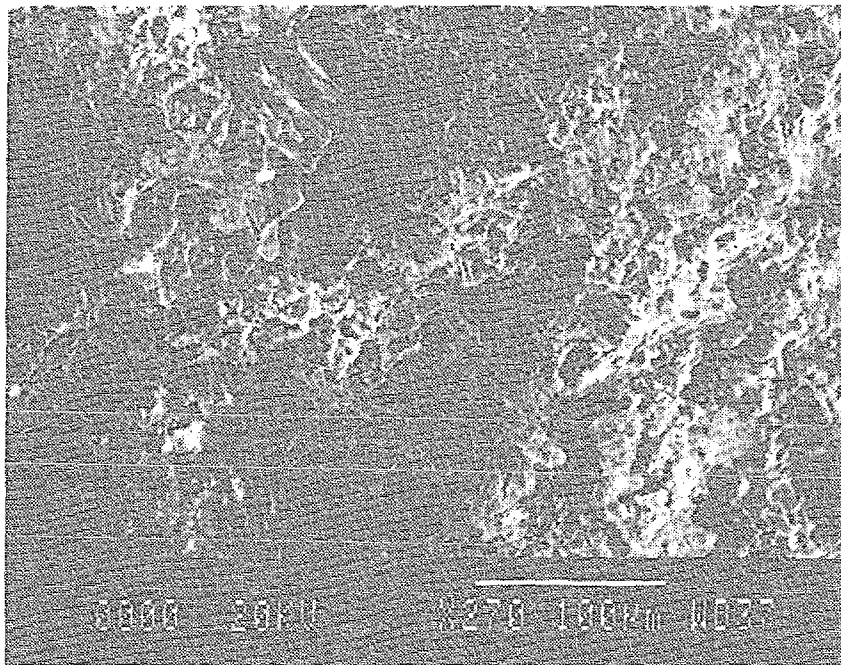


Figure 10: SEM image from sample GP-3

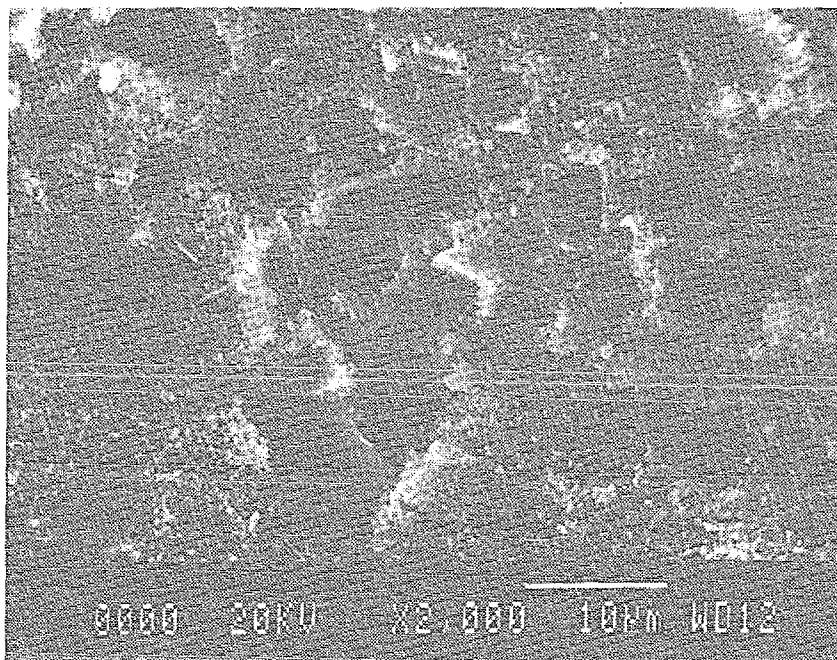


Figure 11: SEM image from sample KP-2

Cement-glass (which can be considered a geopolymer as well) samples showed a kind of structure that can normally be seen in hydrated cements. Unlike other geopolymers, salt crystals from undissolved waste can be clearly seen. This is predictable, since the water in the PAW hardener is hydration water which is not available for dissolving the waste salt. Figure 12 is an SEM micrograph showing a typical salt crystal (70 % Na) that can be seen in S-1 and S-2.

The XRD diffractograms for samples GP(1-5), KP-1, and S-1 are shown in Figures 13 to 15. Only corundum and zirconia sand peaks are clearly identified in GP(1-5) and KP-1 samples. A few more peaks were not identified which are likely to belong to one or more minor zeolite structures.

The pore contents of the samples also depended on their compositions. Table 5 shows the measured open porosity (with Xylol impregnation) for some of the samples and compared with S1 and pure solid Trolit.

Sample	Open Porosity [%]
GP-1	23.1
GP-3	21.9
GP-4	25.3
KP-1	27.8
S-1	8.8
Trolit	21.1

Table 5: Open porosity contents of solidified samples

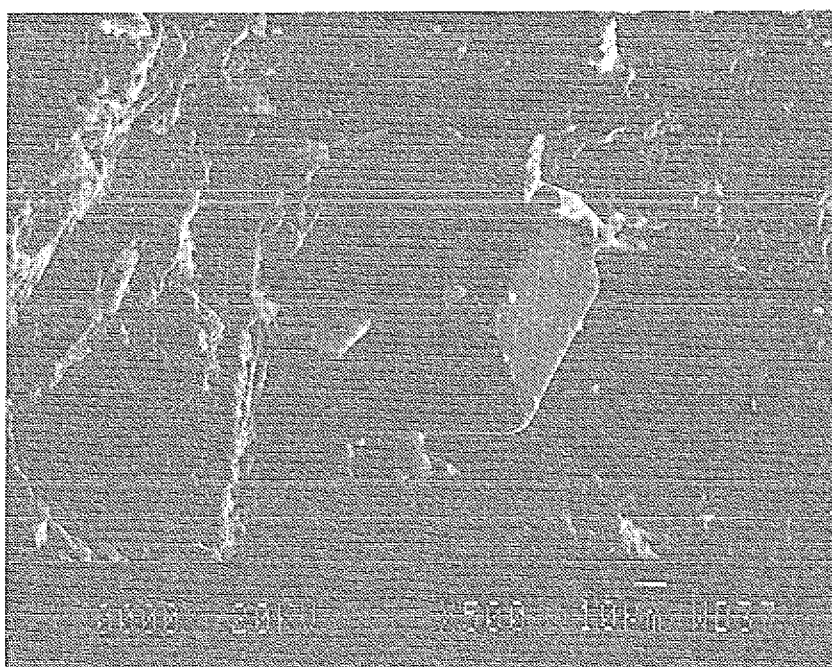


Figure 12: SEM image showing a typical salt crystal in sample S-1

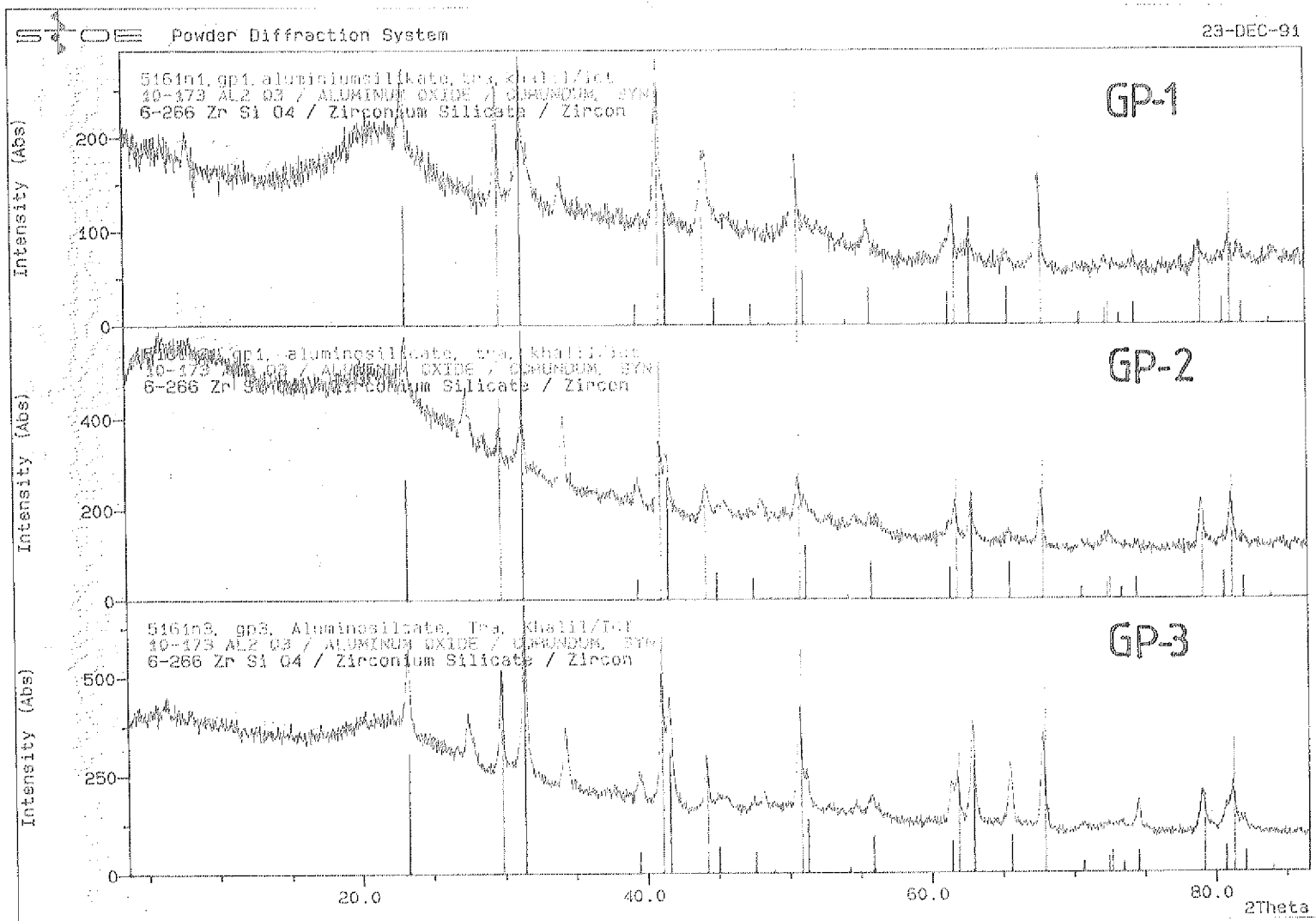


Figure 13: X-ray diffractograms for samples GP (1-3)

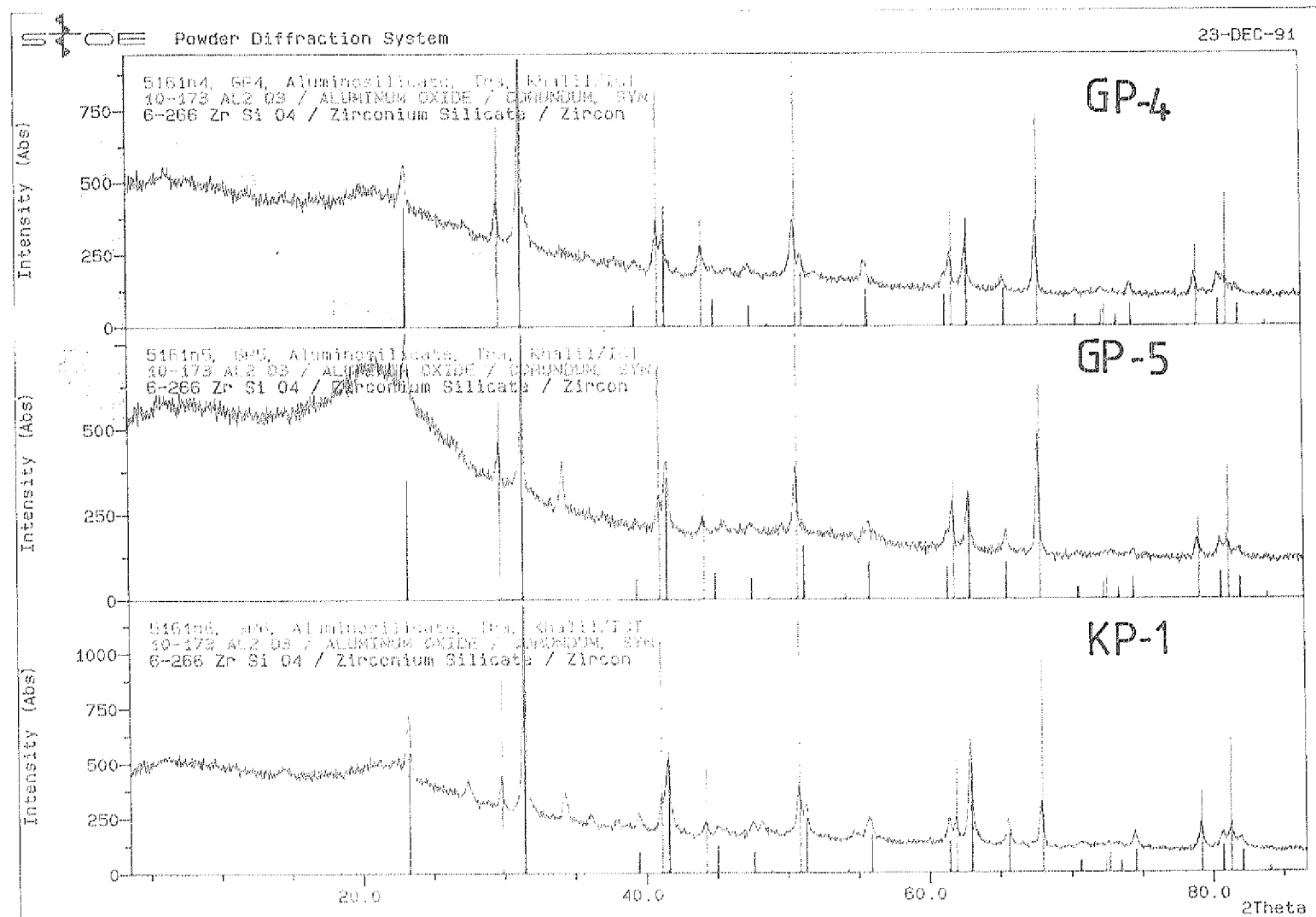


Figure 14: X-ray diffractograms for samples GP (4-5) and KP-1

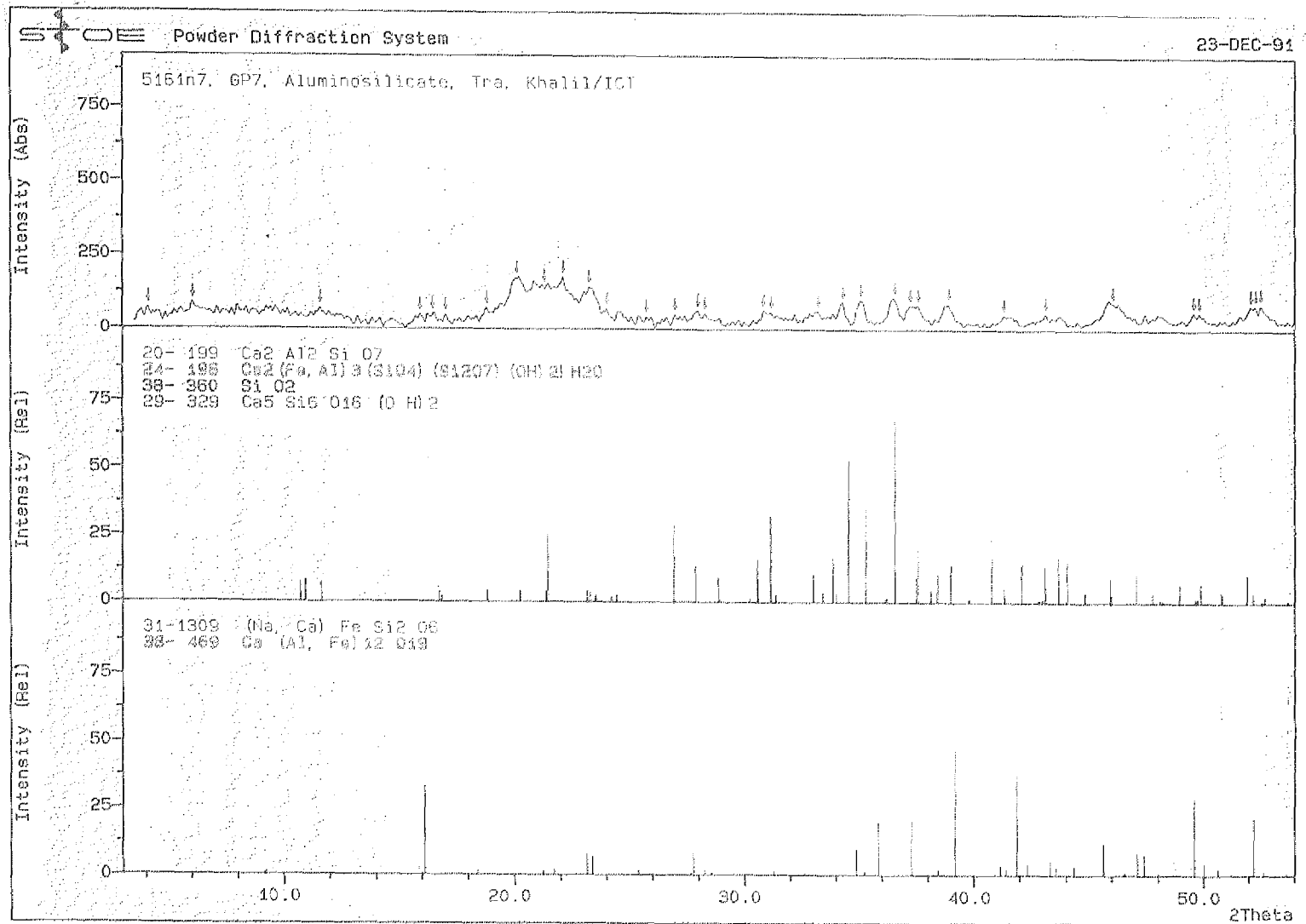


Figure 15: X-ray diffractograms for samples S-1

4.2 Waste Conditioning

The starting composition of the MAW used in this study is given in Appendix A. Other organic constituents that exist in low concentrations were not included. This was justified by the intention of studying the effect of such high sodium contents on the solidification process and the retention of specific important elements such as Cs, Sr, Tc, and U in the solidified matrix.

Using the waste in its solution form was neither desirable nor possible. There was no need to keep such a large volume of water when it is not important for the solidification reaction as in the cement matrix, for instance. Also, diluting the hardener to that extent changes the conditions necessary for geopolymerization. Therefore, the waste solution was dried slowly at low temperature (80°C) before solidification.

Since nitrates of the component elements were used for preparing the simulated MAW solution, in addition to a large amount of free nitric acid, the solution had a pH of about 1. Hence, three different solutions were prepared from the original one for the drying process.

- a) Waste solution denitrated with formaldehyde which contained a slight extra quantity of formaldehyde and then neutralized with NaOH (named MW1).
- b) Waste solution denitrated with formaldehyde which contained a slight extra quantity of free nitric acid and was then neutralized with NaOH (MW2).
- c) Waste solution without denitration or neutralization (MWO).

These solutions were dried batchwise in glass beakers of 1 liter, over a hot plate with continuous stirring. After most of the water was lost, the sludge was moved to a drying oven at 100°C for a few days.

Geopolymer systems with KOS, ROS, and KAO failed to solidify when mixed with either MW1 or MW2. Therefore, these two preparations were discarded and only MWO was used in the study.

4.3 Waste Loading and Sample Preparation

4.3.1 Waste Loading

Preliminary experiments were performed to maximize waste loading in the geopolymer system. In these experiments only the reactive components KOS and ROS in addition to the hardener were varied while using equal weights of hardener and reactive component. The

results for KOS and ROS were similar in that a hard solid product was not formed when the MWO/reactive component ratio was greater than 0.5. It was also noticed that those samples which formed a monolith at ratios < 0.5 did not obtain strength equal to that of the unloaded material with other additives. When other nonreactive components (additives) of the geopolymer system were added while maintaining the MWO/reactive component ratio below 0.5, the samples gained less strength than that of geopolymer matrix described in an earlier section.

Since the reactive component is about 30 % by weight of the total solid part of the geopolymer, the loading ratio has to be kept below 15 % of the solid component. However, using MWO/(solid + hardener) ratios of 10 and 15 % (the values that appear in Table 3) produced high strength samples. This indicates that the nonreactive part of the geopolymer system also plays an important role in the final strength of the products.

4.3.2 Sample Preparation

4.3.2.1 MAW Samples

All samples loaded with simulated MAW (MWO) were prepared by first mixing the TROLIT and the hardener according to the ratios shown in Table 1. The dry and ground waste simulate MWO was then added and mixed for several minutes. Samples GP-1 and GP-2 had the usual viscosity of a freshmixed geopolymer. Samples GP-3 were quite hard to mix because of the reduced hardener ratio. This is an important factor when considering a large-scale solidification process. Samples GP-4 and GP-5 were easy to mix because of the extra hardener in the first and the reduced reactivity of the hardener used in the second, which took a longer time to start the hardening reaction.

On the other hand samples KP-1 (which resemble GP-1) were hard to mix owing to the fact that the finer grains of KOS reactive components speeded up the hardening reaction. With 15 % MWO samples KP-2 (which resemble GP-2) could not be mixed with only 30 % hardener and another 10 % had to be added.

Mixtures of TROLIT (or SECAR 51) and MWO were poured in to polyethylene containers which were slightly conical with large and small diameters of 1.95 and 1.83 cm, respectively, and 2.24 cm high. The containers were closed with their own caps, and placed at room temperature. All samples formed hard monoliths in the time between 20 min. and 2 hours. After one week samples were placed in a drying oven at 80°C. After 4 days the containers were removed and the solid samples were kept at 80°C for 3 more days before being used for leaching experiments.

The geopolymer matrix usually rejected the extra water produced in the hardening reaction. With waste mixed in the samples, this appeared as a white precipitate on the surface of the solid samples and outside the polyethylene container after one day at 80°C. Some of this precipitate were collected for analysis. The quantity of precipitate on the surface varied between samples. Samples with less hardener or a less porous structure gave less precipitates. Samples S-1 and S-2 had very little to no precipitate on the surface.

4.3.2.2 Technetium Samples

Samples containing technetium were prepared in a very similar fashion to those containing MAW. They contained 10 % by weight MWO. In addition, 0.488 g of NH_4TcO_4 (as the only available form of Tc-99) was added to a batch of 90 g TROLIT plus hardener and 9 g MWO. The technetium was added to the hardener which was then mixed with the TROLIT and MWO for a few minutes, before pouring into polyethylene containers. Heating the samples to 80°C, small amount of a white precipitate appeared on the surface similar to the others. Geopolymer samples containing technetium were coded TG-.

4.3.2.3 Uranium Samples

Three types of geopolymer containing uranium samples were prepared as follows:

1. Samples containing 3 % by weight uranium in the form of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. These were prepared by mixing first the hardener and uranium compound, then the TROLIT was added and mixed for a few minutes (Coded NG-..)
2. Samples containing 10 % MWO in addition to 0.04 % uranium in the form of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. In this case the uranium compound was mixed with the MWO then with the TROLIT before adding the hardener (coded NW-..)
3. Samples containing 10 % U_3O_8 added to the mixture of TROLIT and hardener (coded OG-..).

The uranium samples were treated similarly to the other samples with regard to curing procedure. In all cases the samples showed very little white precipitate on the surface.

4.4 Leaching Experiments

Static leach tests of the geopolymer matrix were performed in two solutions; distilled water and Q-brine. Before the start of the leaching experiments, samples were weighed, dimensions measured, and washed in distilled water for 15 seconds. Table 6 gives the weight, and calculated density for each samples. Since each experiment was made of duplicates, each sample has the letter A or B next to the sample code.

While all samples including those containing Tc or U had almost the same volume, different leachant volumes, and solution sample volumes were used. These were decided on the basis of the following analysis techniques. In all cases, except the technetium samples, the solution sample was replaced with an equal volume of fresh leachant. The calculated density is also given in Table 3. Density is dependent not only on the sample composition, but also on the volume of air trapped.

Samples containing nonradioactive waste were all leached at room temperature (20-22°C), while those containing Tc or U were leached at 50°C. Again, the choice here is related to the analysis technique. While solution samples containing radioisotopes were prepared instantly and counted within a few hours, the others had to wait for the availability of analysis equipment. If the solution samples were originally at higher than room temperature, there is a possibility that some elements might precipitate when cooled. Table 6 gives also the running temperature for all samples.

Sample Code	Sample [weight]	Calculated Density [g/cm ³]	MWO [wt.-%]	Leachant Volume [ml]	Leachant Sample [ml]	Temp. [°C]
GP-1A	15.395	2.37	10	500	10	Room
GP-1B	15.860	2.44	10	500	10	Room
GP-2A	15.053	2.31	15	500	10	Room
GP-2B	15.223	2.34	15	500	10	Room
GP-3A	16.557	2.54	10	500	10	Room
GP-3B	16.926	2.60	10	500	10	Room
GP-4A	14.469	2.22	10	500	10	Room
GP-4B	14.357	2.21	10	500	10	Room
GP-5A	15.740	2.42	10	500	10	Room
GP-5B	15.624	2.40	10	500	10	Room
BG-12	17.314	2.66	-	500	10	Room
BG-3	18.790	2.89	-	500	10	Room
BG-4	16.790	2.58	-	500	10	Room
BG-5	14.872	2.28	-	500	10	Room
KP-1A	15.188	2.33	10	500	10	Room
KP-1B	15.360	2.36	10	500	10	Room
KP-2A	14.559	2.24	15	500	10	Room
KP-2B	14.580	2.24	15	500	10	Room
BK-12	16.639	2.56	-	500	10	Room
S-1A	14.576	2.28	10	500	10	Room
S-1B	14.189	2.22	10	500	10	Room
S-2A	14.474	2.24	15	500	10	Room
S-2B	14.238	2.20	15	500	10	Room
BS	14.872	2.30	-	500	10	Room
GQ-1A	15.455	2.37	10	50	1	Room
GQ-1B	15.508	2.38	10	50	1	Room
GQ-2A	14.931	2.29	15	50	1	Room
GQ-2B	15.105	2.32	15	50	1	Room
GQ-3A	16.458	2.53	10	50	1	Room
GQ-3B	16.552	2.54	10	50	1	Room
GQ-4A	14.469	2.22	10	50	1	Room
GQ-4B	14.914	2.29	10	50	1	Room
GQ-5A	14.947	2.30	10	50	1	Room

GQ-5B	14.951	2.30	10	50	1	Room
KQ-1A	14.814	2.28	10	50	1	Room
KQ-1B	14.920	2.29	10	50	1	Room
KQ-2A	13.920	2.14	15	50	1	Room
KQ-2B	13.935	2.14	15	50	1	Room
SQ-1A	13.292	2.22	10	50	1	Room
SQ-1B	14.367	2.23	10	50	1	Room
SQ-2A	14.325	2.23	15	50	1	Room
SQ-2B	14.468	2.25	15	50	1	Room
OG-QA	17.323	2.66	10 [*]	200	2	50
OG-QB	17.234	2.65	10 [*]	200	2	50
OG-H	16.981	2.61	10 [*]	200	2	50
NG-QA	15.378	2.36	3 ⁺	200	2	50
NG-QB	15.360	2.36	3 ⁺	200	2	50
NG-HA	15.021	2.31	3 ⁺	200	2	50
NG-HB	14.466	2.22	3 ⁺	200	2	50
NW-QA	15.578	2.39	10 ^{\$}	200	2	50
NW-QB	15.449	2.37	10 ^{\$}	200	2	50
NW-HA	15.449	2.37	10 ^{\$}	200	2	50
NW-HB	15.369	2.36	10 ^{\$}	200	2	50
TG-QA	16.101	2.47	10 [£]	200	0.1	50
TG-QB	15.715	2.41	10 [£]	200	0.1	50
TG-HA	15.779	2.42	10 [£]	200	0.1	50
TG-HB	15.829	2.43	10 [£]	200	0.1	50

* No MWO, only U as U₃O₈

+ No MWO, only U as UO₂(NO₃)₂ · 6H₂O

\$ MWO + 0.04 wt % U as UO₂(NO₃)₂ · 6H₂O

£ MWO + 0.3 wt % Tc as NH₄TcO₄

Table 6: Sample Parameters and Leaching Conditions

5. RESULTS AND DISCUSSION

5.1 Solution Analyses

Water samples without radioisotopes were analyzed with an ICP-MS. This technique is sensitive to less than 1 ppb for most elements. Therefore, despite the large volume of the leachant compared to the solid sample, the level of sodium in solution was too high for the equipment. Hence, samples had to be diluted 1:2 before analysis. Sampling time was 7, 35, 65, 93, 121, 178 and 210 days, and solutions were analyzed for Sr, Cs, Mo and Si.

Q-brine samples with no radioisotopes were analyzed using an ICP technique. This was proved to be a difficult task even after diluting the samples 1:20. Nor was it not possible to use the ICP for Cs analysis. Therefore, the same diluted solutions were used for AAS analyses of Cs. However, signal interference from K and Na with Cs caused the accuracy to be reported as 30 %; while the detection limit is about 10 ppb.

On the ICP, samples were analyzed for Sr, Mo, and Si. The detection limits for these elements were set as 1 ppb, 1 ppb, and 10 ppb, for Sr, Mo, and Si, respectively. Leach experiments in Q-brine ran for 6 months and samples were taken after 7, 37, 65, 93, 121, 182 days.

Analyses for technetium were done using the liquid scintillation technique. Since it is the only radioisotope in solution (in addition to K-40), separation was not necessary. The efficiency of the technique for detecting technetium is 95 % for both water and brine solutions using Quicksafe-A liquid scintillator. When about 1 ml of HCl was added the efficiency dropped to 92 %, as determined using the standard. Quicksafe-A was able to form a clear homogeneous solution with both water and Q-brine up to 2 ml/17 ml of scintillator with no problem. Nevertheless, in most measurements only 100 μ l was needed in 19 ml of liquid scintillator. Solution samples were taken after 7, 28, 56, 84, 113 and 136 days from the start of leaching.

The liquid scintillation technique was also used for uranium analysis, taking advantage of its alpha activity. Two ml of solution was added to 17 ml of Quicksafe-A. This gives a clear mixture that was counted for 2 hours. The volume of leachant taken was always replaced with 2 ml of fresh solution. The dilution caused by this process was accounted for during analysis calculations. In Q-brine solutions the K-40 peak always interfered with the alpha peak from U. Only alpha peaks that appear on top of the K-40 β continuum were considered by subtracting the β part as a background. This is illustrated in Fig. 16. Using this procedure, uranium activity in solution as low as 0.1 Bq was detectable. This corresponds to a uranium

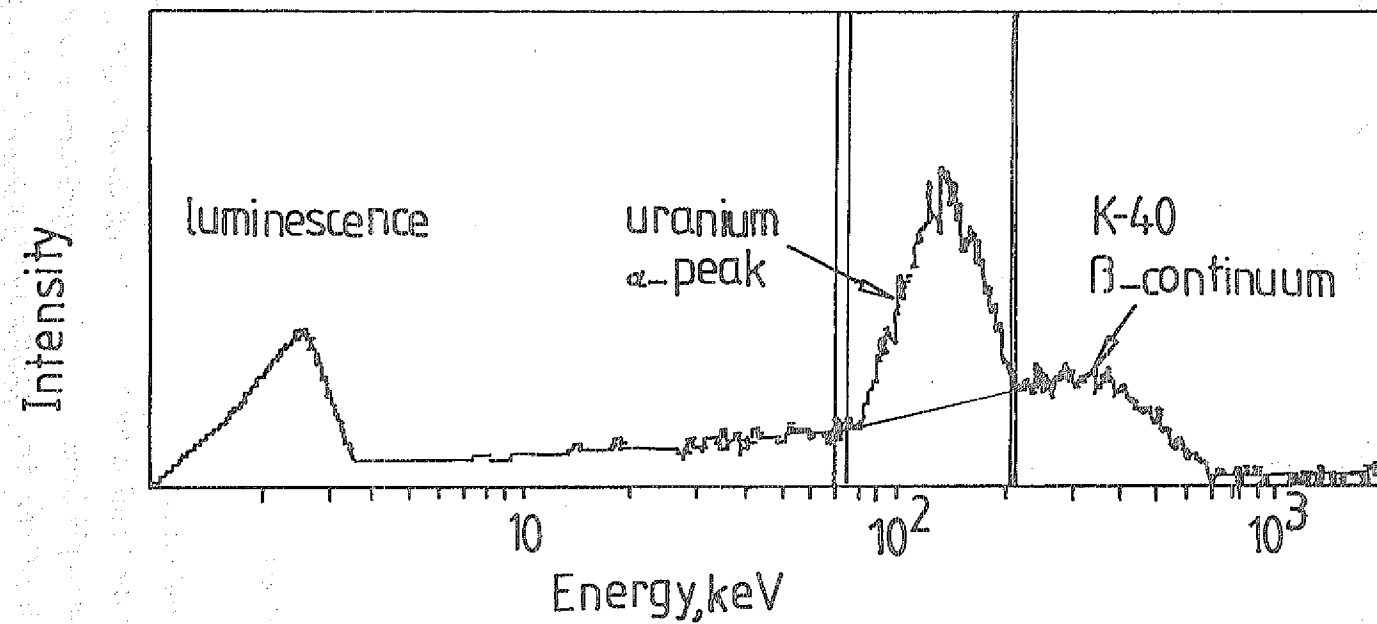


Figure 16: Uranium α -scintillation peak on top of K-40 β continuum

weight of about 8 μg in the solution sample volume. In other words, the detection limit is about 4 $\mu\text{g}/\text{ml}$ since 2 ml was used every time. The K-40 β continuum problem was not encountered in technetium detection since the latter had relatively high peaks.

5.2 Sample Behavior in Solution

In MAW leaching experiments samples were suspended in the distilled water at room temperature. All samples were visually intact until the end of the leaching period. Samples GP-2, GP-3, and GP-5 colored their solutions pale yellow in about 24 hours. This probably comes likely from the leaching of Fe and Cr ions. It is also consistent with the high Fe content of these samples shown in Table 4. None of the water samples showed any change in volume or shape. Samples GP-2 and GP-4 had a few pieces about 1-3 mm broken off. The pH of the solutions was measured at the end of the leaching period and given in Table 7. Also given, for comparison, the pH of solutions in which blank samples were leached for the same time. All pH values were measured with an Ag/AgCl glass electrode.

Sample Code	pH Sample	pH Blank
GP-1	9.5	9.5
GP-2	11.4	9.5
GP-3	11.2	8.6
GP-4	9.7	9.6
GP-5	11.3	8.4
KP-1	11.2	11.2
KP-2	11.4	11.2
S-1	11.4	11.0
S-2	11.4	11.0

Table 7: pH of water at the end of leaching experiments (210 days)

Again, samples GP-1 and GP-4 stand out as causing almost no change in the pH of the leachant, compared to the blank solutions. Hence, in samples GP-1, and GP-4 as well as in the blanks, the increase in pH from that of the distilled water is caused by the dissolution of excess or nonreacting hardener. The increase in pH caused in other samples is likely to be the result of leaching out of excess sodium and potassium hydroxides from the hardener. Sodium from the waste loading helped in increasing the nonreacting hydroxides. This idea is supported by the fact that almost the same pH values were measured one week from the start of

leaching. In other words, the leaching of waste components or even hardener that was not in direct contact with the solution might have contributed very little to the pH change.

The tolerance of the samples to the brine solution ranged between poor and very good, based on the composition. Samples were visually examined occasionally during the leach experiments. All changes took place between one and four weeks from start of leaching. At the end of the experiments the samples were checked again and the pH was measured.

Table 8 gives the final pH values (measured with an Ag/AgCl glass electrode), and the final condition of the samples; those which had no cracks also showed no change in dimensions.

Again, samples GQ-2, GQ-3, and GQ-5 colored the solution pale yellow, which is also due to Fe and Cr ions.

Sample Code	pH	Sample Condition
GQ-1	5.3	Several cracks, few little pieces fallen
GQ-2	5.5	Solution pale yellow, fine powder off
GQ-3	5.6	Solution pale yellow, fine powder off
GQ-4	5.3	Several wide cracks, little pieces off
GQ-5	5.5	Samples intact
KQ-1	6.1	Few cracks
KQ-2	6.0	Samples intact
SQ-1	6.7	Samples intact
SQ-2	6.8	Samples intact
brine	5.0	-

Table 8: pH values and sample conditions at the end of Q-brine experiments (182 days)

Except for GQ-4, GQ-5, and KQ-2, all other samples showed a white precipitate on the bottom of the leach container. This precipitate proved to be leached out sodium silicate which had exceeded its solubility limit in the brine. This point will be discussed further in the next section. It is also relevant to notice that, while all samples raised the pH of the brine, samples GQ-2 and GQ-4 did so least. It is also important to remember here that the white precipitate on the surface was not washed off the solid samples before leaching in the brine.

The cracking of samples in brine solution can be attributed to the presence of a relatively high concentration of chlorine ions. The alkali metal ions (Na and K) and the alkaline earth ions

(Sr and Mg) are unlikely to cause any damage to the geopolymer structure. On the contrary, these elements form the stabilizing ions around which the network of SiO_4 and AlO_4 tetrahedra are linked, as explained in previous section. Since the sulfate ion SO_4^{2-} also exists in Q-brine, one might suspect that it has also an effect on the geopolymer structure.

Therefore, three pieces of the same sample of geopolymer (composition of GP-1) with no waste loading were soaked in concentrated H_2SO_4 , HNO_3 and HCl at 50°C . The sulfuric acid and nitric acid had almost no effect on the integrity of the geopolymer, even after soaking for 10 days. The hydrochloric acid was very devastating, though. Most of the sample soaked in HCl was turned into powder in less than 24 hours.

This simple test led to the belief that chlorine is effective in attacking the geopolymer structure. The affinity of chlorine to react with sodium causes destabilization of the structure. As the Na ion is attracted out of the cage of tetrahedra (or the chlorine ion is attracted in), a charge imbalance is effected. This leads to reformation of the network, which causes excess internal stress that results in cracking of the sample.

Geopolymer samples containing technetium were tolerant to water. At the end of the leaching experiments (136 days), samples were visually intact and did not change dimensions. On the other hand, samples were very intolerant to the brine solution. They had many cracks after one day of soaking. After one month they were broken into many pieces. The break up of samples can be explained in terms of the chemistry of technetium used. When NH_4TcO_4 was added to the TROLIT hardener it reacted with the KOH forming KTcO_4 . This precipitated inside the hardening matrix under the effect of the alkalinity of the system. As a result there were regions of incomplete reaction, which are characterized by being weaker than the rest of the sample. Stresses that resulted from the action of Q-brine on the geopolymer matrix broke the samples at those weak regions. The solubility of KTcO_4 in water caused the fast leaching of all Tc into solution as will be explained in the next section.

Geopolymer samples containing uranium were also tolerant to water. Similar to the MAW and technetium samples, their tolerance to brine solution was poor. Unlike samples of other compositions reddish spots about 1 mm in diameter developed here on the surface. They also showed the same color around the cracks. When one samples was broken at the crack, the color was found to extend across, but not uniformly through the cross section. This is the Fe content of the TROLIT part of geopolymer that was oxidized after some time in Q-brine. In summary, the tolerance of uranium samples to brine solution was similar to the MAW samples and less severe than the technetium ones.

5.3 Results and Discussion

Results from the analysis of Q-brine samples are given in Figs. 17, 18, 19, and 20 for Mo, Sr, Cs, and Si respectively. The first three were expressed as percentage fractions of the element that was leached into solution. It was possible to calculate this since these elements only existed in

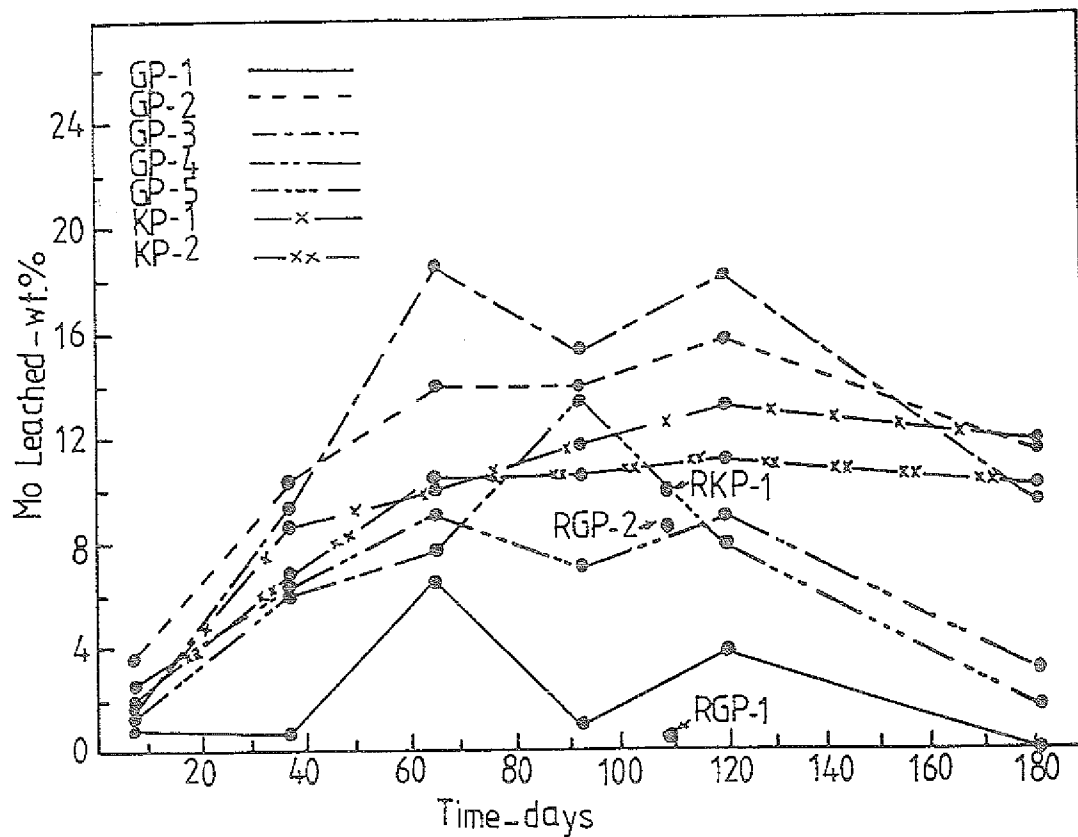


Figure 17: Mo fraction leached (wt.-%) in Q-brine

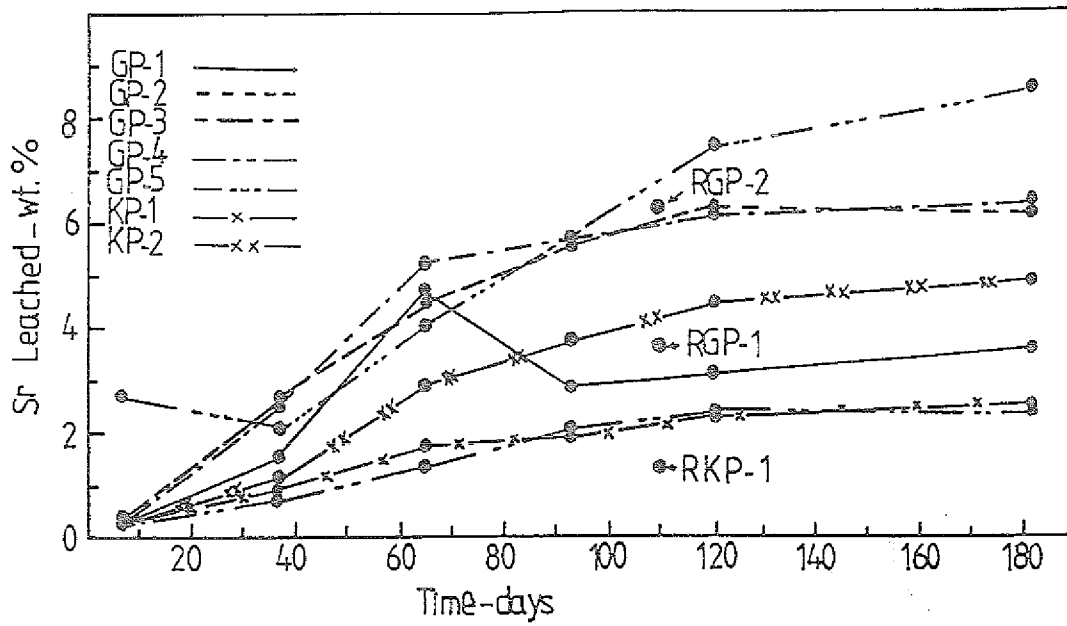


Figure 18: Sr fraction leached (wt.-%) in Q-brine

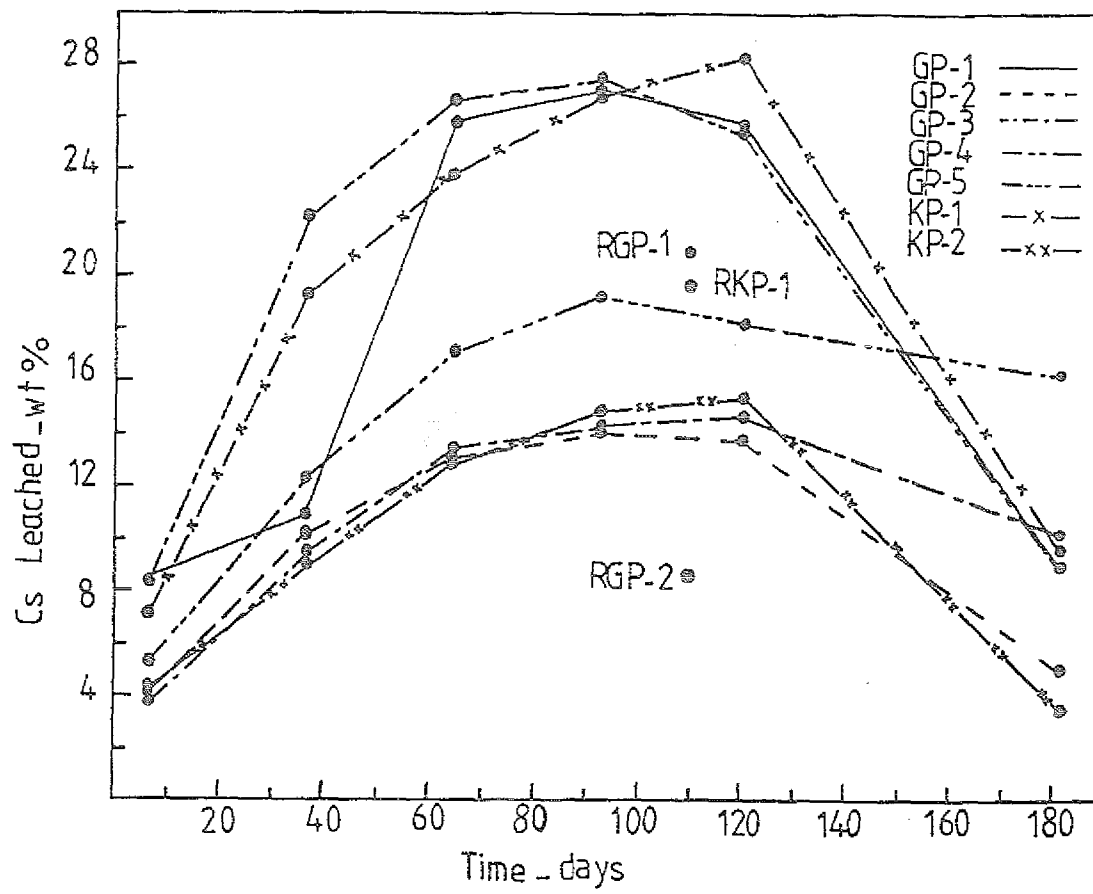


Figure 19: Cs fraction leached (wt.-%) in Q-brine

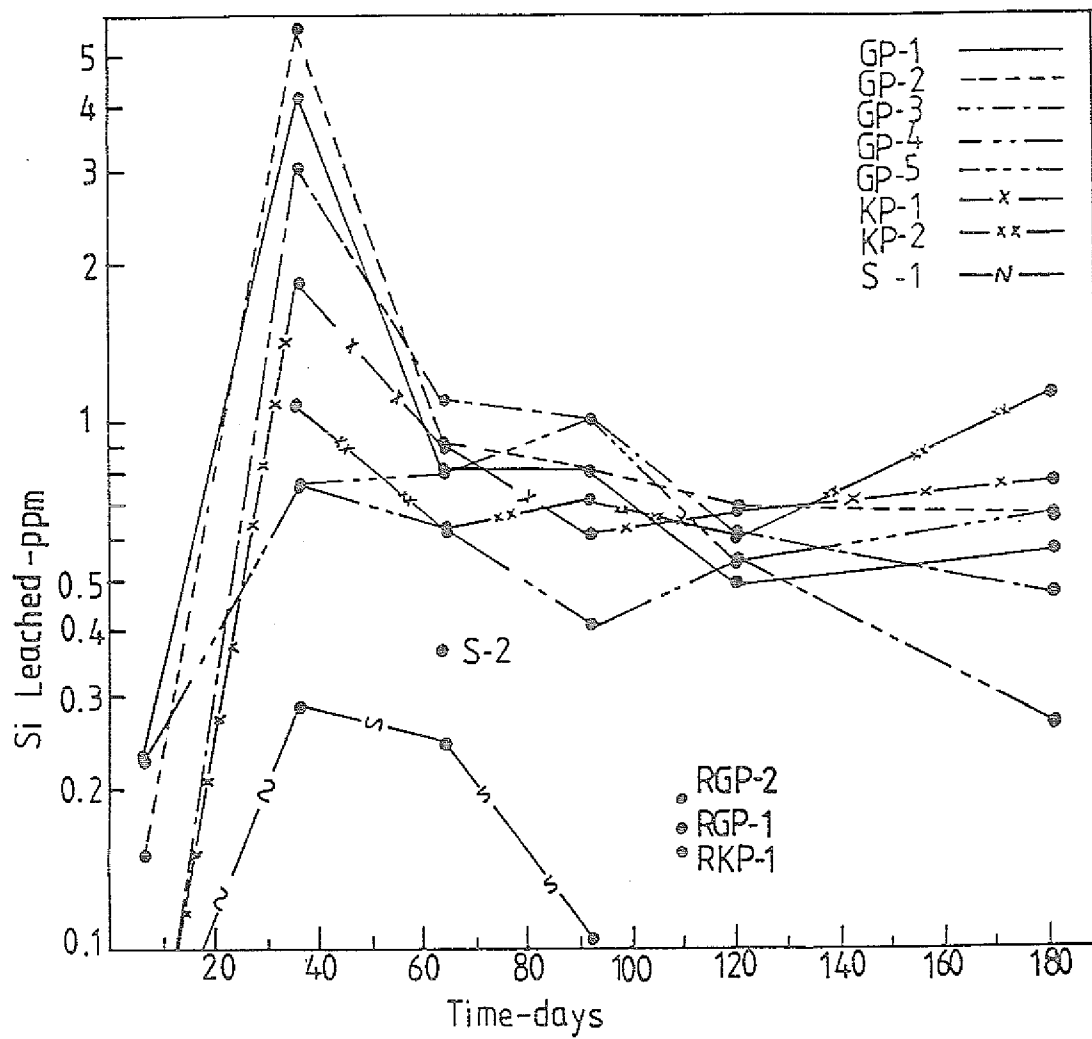


Figure 20: Si concentration in Q-brine, ppm

the waste loading. On the other hand silicon in solution could have come from the nonreacted hardener, the matrix, or the waste. Since it is not possible to discriminate between the different sources of Si, it is plotted as $\mu\text{g/ml}$ versus time. Sr, Cs, and Mo concentrations in solutions of samples SQ-1 and SQ-2 were below the detection limit. In other words, leached fractions from SQ-1, for instance, were less than 0.27 wt.%, 3.6 wt.%, and 0.01 wt.%, for Sr, Cs, and Mo, respectively, during the 6 months of soaking.

Results from water leaching experiments were different from those in brine solutions. Sr was not detectable in any sample. All other elements (Cs, Mo, and Cr) showed a constant concentration from the start of the sampling (after 7 days) to the end of the available data. Results for leaching experiments in water are shown in Figs. 21 and 22 for Cs and Mo, respectively. On the one hand, the Mo fraction leached in water has about double the fraction leached in Q-brine. This can be true only when no ion exchange process is taken place for Mo leaching. On the other hand, less Cs was leached in water than in Q-brine. A good indication that Cs leaching involved an ion exchange between the solid and solution systems.

Only Cs had appeared in detectable concentrations in the cement-glass solutions. Some geopolymer compositions showed more retention for Cs than cement-glass. This is predictable from previous experience of Cs behavior in a cement matrix (29).

Silicon concentration in solution has almost the same pattern for all experiments in Q-brine. Concentrations increase rapidly to reach a maximum value after about 30 days from the start. Then, they decrease gradually and converge to approximately the same value. This value is the solubility limit of the silicon compound (likely sodium silicate) at that temperature and pH in brine. Not only the curves in Fig. 20 suggest that but also the white precipitate at the bottom of the leaching containers. These white precipitates first appeared as clouds in solutions, then started to precipitate giving again clear brine. In water samples, silicon was not analyzed, nor was there any visible precipitate in solution.

Other elements (Sr and Mo for that matter) did not behave similarly to silicon in brine solution. In other words, their concentrations in solution increased slowly to reach a certain equilibrium in about 60 days. Cs concentration increased slowly to reach a maximum after 121 days then decreased from then on. In combination with the silicon data (and water data) one can conclude that most of the Sr and Cs was not part of the nonreacted hardener. The data also suggest that these elements were part of the solid structure. The fraction of these elements that was not part of the structure dissolved first giving the initial rise in concentration in both solutions (water and Q-brine). In water that part of the curve was fast and took place in less than a week. There was no further leaching in water since it required enough ions for the exchange of

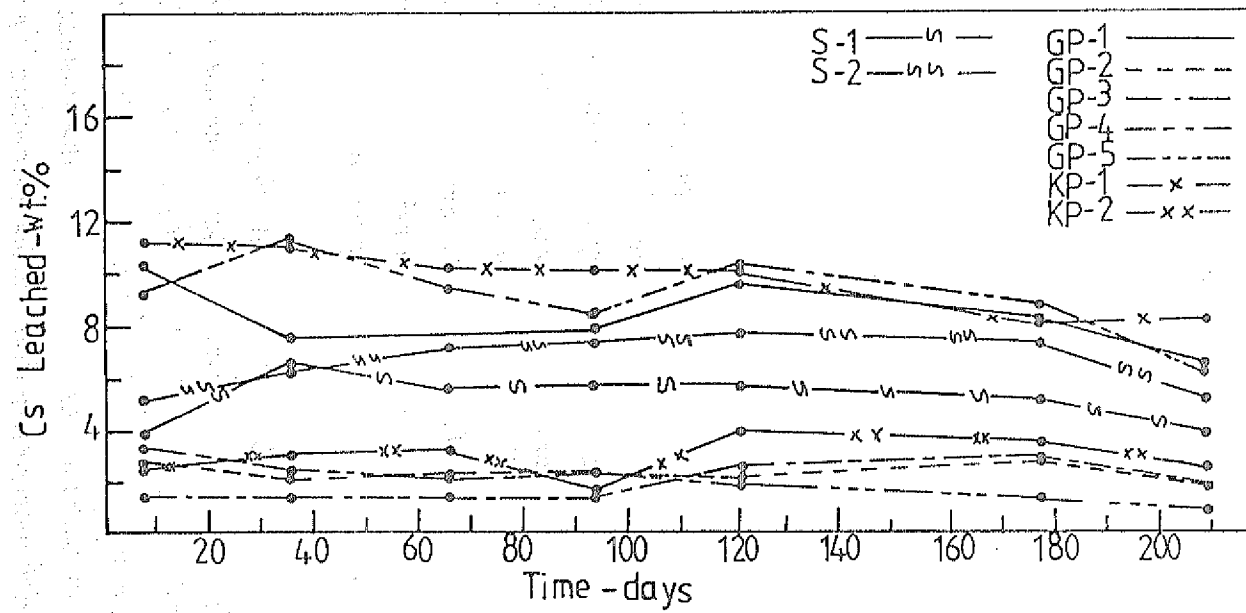


Figure 21: Cs fraction leached (wt-%) in water

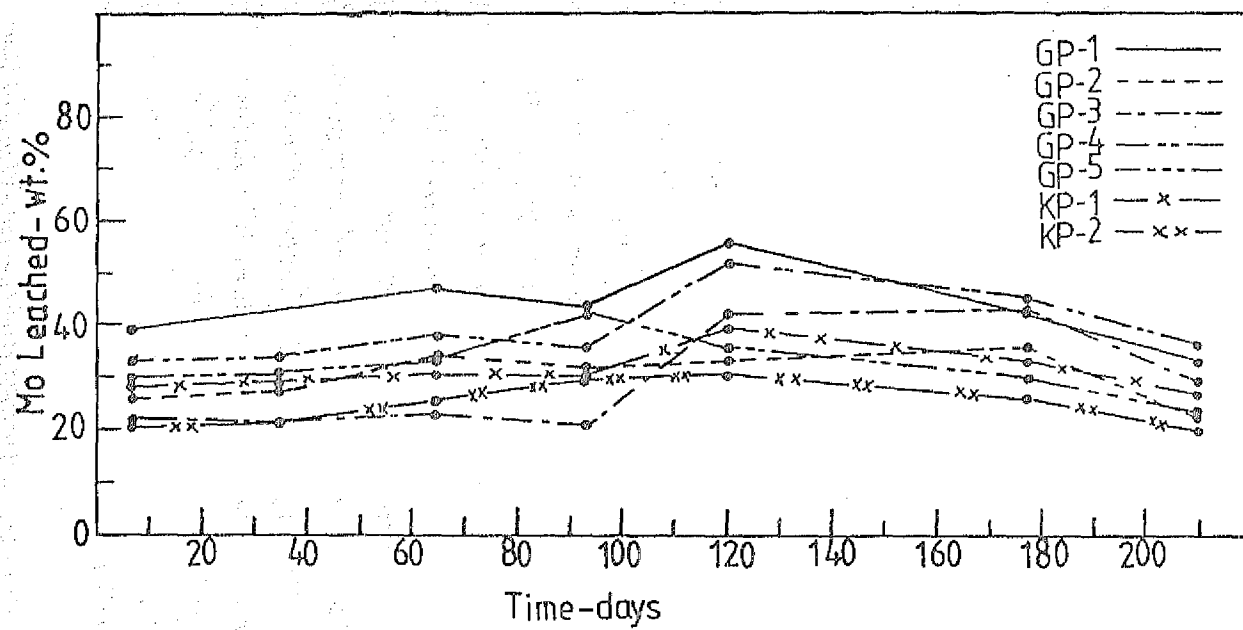


Figure 22: Mo fraction leached (wt-%) in water

sites with the elements caged in potassium (and also magnesium) to exchange sites like a zeolite in keeping certain cations and exchanging them when necessary with those in solution. In the case of Cs, the only alkali metal cation available, this process was reversible which explains the decline in the last part of the Cs concentration curve.

As explained earlier, the structure of samples QG-1 (resembles GP-1) and QG-4 (resembles GP-4) was different from those of other geopolymer compositions investigated. Therefore, their preference for exchanging certain elements is different as well. Hence, while their retention of Sr was higher than all other compositions, they released Cs at a much higher rate.

Three samples of the type GP-1, GP-2, and KP-1 were each placed, in 15 ml of Q-brine in a polyethylene container and exposed to a gamma dose of $1E7$, $1E8$, $1E7$ rads, respectively. Including irradiation time, samples were soaked in the Q-brine for 110 days. Samples of the brine were then analyzed for Mo, Sr, Cs, and Si. The results are shown as one point (each) in Figs. 17, 18, 19, and 20, respectively. These points are referred to as RGP-1, RGP-2, and RKP-1. Gamma irradiation appears not to affect the leaching rate or the integrity of the samples any further than the Q-brine itself. For silicon analysis the three points are very close, which is not surprising since its concentration in Q-brine is controlled only by the solubility limit of sodium silicates.

In either water or brine solution, technetium was leached rather quickly. In water almost 100 % of the technetium was in the solution after 1 week, despite the fact that the samples were visually intact. In Q-brine, controlled only by its solubility rate constant, it took about one month for almost all the technetium to go into solution. Because of the possibility of the inhomogeneous distribution of technetium in the samples, the total technetium in each experiment was calculated. At the end of leach experiments, the solid samples (or their pieces) were washed and dissolved in concentrated HCl. The solution was counted and the technetium amounts in the solid calculated and added to the average technetium in solution. The latter was calculated based on all six measurements in water and only the last four measurements in Q-brine. Fig. 23 shows the fraction of technetium leached from the geopolymer matrix in both water and Q-brine at 50°C versus leaching time. Since a large quantity of technetium was loaded in each sample, almost 66 mg, and only 2-4 % remained on the solid, it is not clear whether there is any upper limit for technetium loading in geopolymer. When that limit is exceeded, the extra material is not incorporated in the matrix.

The results from uranium leaching experiments are shown in Figs. 24 and 25 for water and Q-brine, respectively. In water the fraction of uranium leached from samples NW-H increased rapidly to stabilize after almost two months at about 36 wt.-%. Similar samples (NW-Q) gave

no measurable concentration in brine solution. Samples OG-H and OG-Q were leached the same way in both water and brine to stabilize at almost 0.6 % leached fraction after about 80 days. NG-H samples gave a uranium concentration below the detection limit in water. Also, in brine solution the concentration was very low and appeared above the detection limit only after 130 days. The leaching of U_3O_8 from the solid phase is slow due to its own dissolution kinetics. Samples NW-H and NW-Q are most interesting. They represent an actual case of ILW (MAW) contaminated with heavy metal. Uranium in such combination is highly leachable in water, and less leachable in Q-brine. Uranyl nitrate by itself was not leachable. This can be attributed to the chemistry of the product of uranyl nitrate reaction with the alkaline hardener. From the waste solidification stand point, ILW contaminated with uranium and solidified in aluminosilicate binder is likely to release uranium at a high rate especially in water.

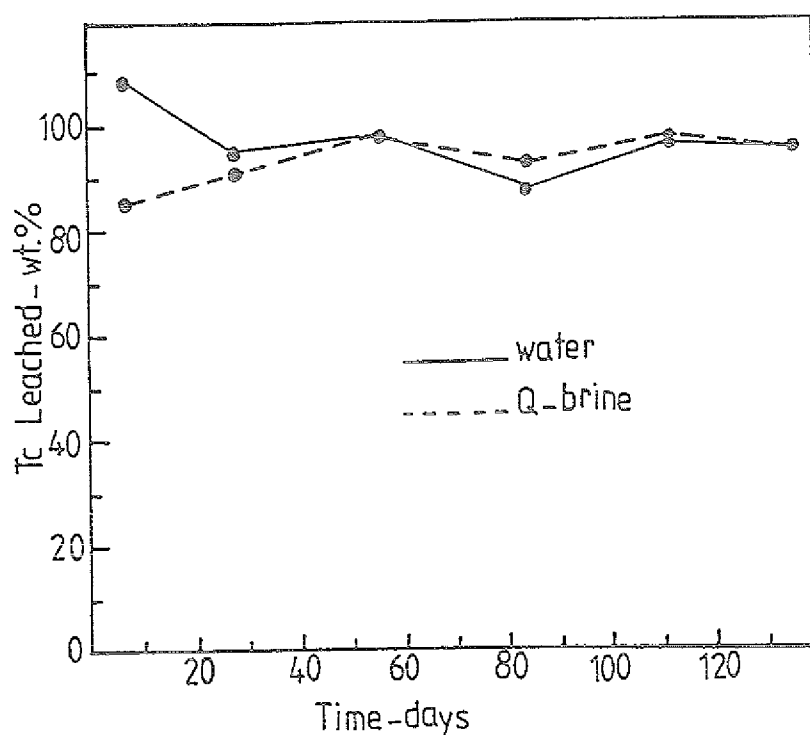


Figure 23: Tc fraction leached (wt.-%) in water and Q-brine at 50°C

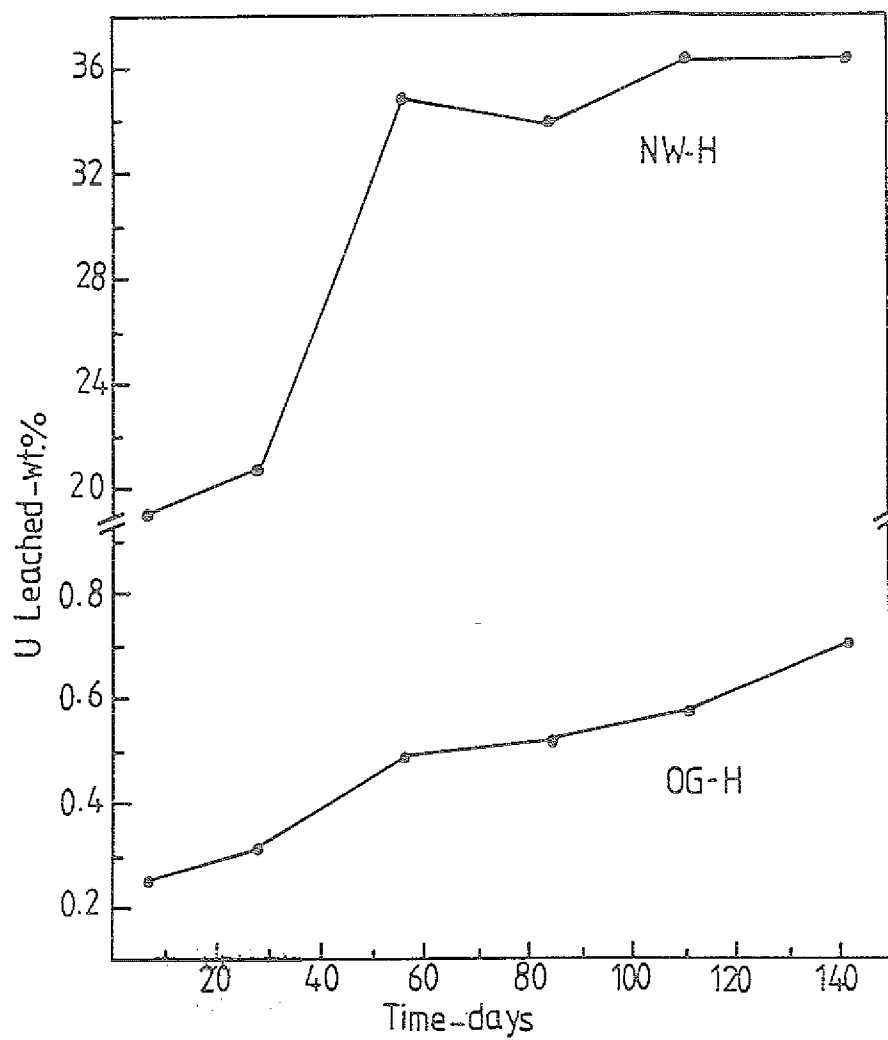


Figure 24: U fraction leached (wt.-%) from samples NW-H and OG-H in water at 50°C

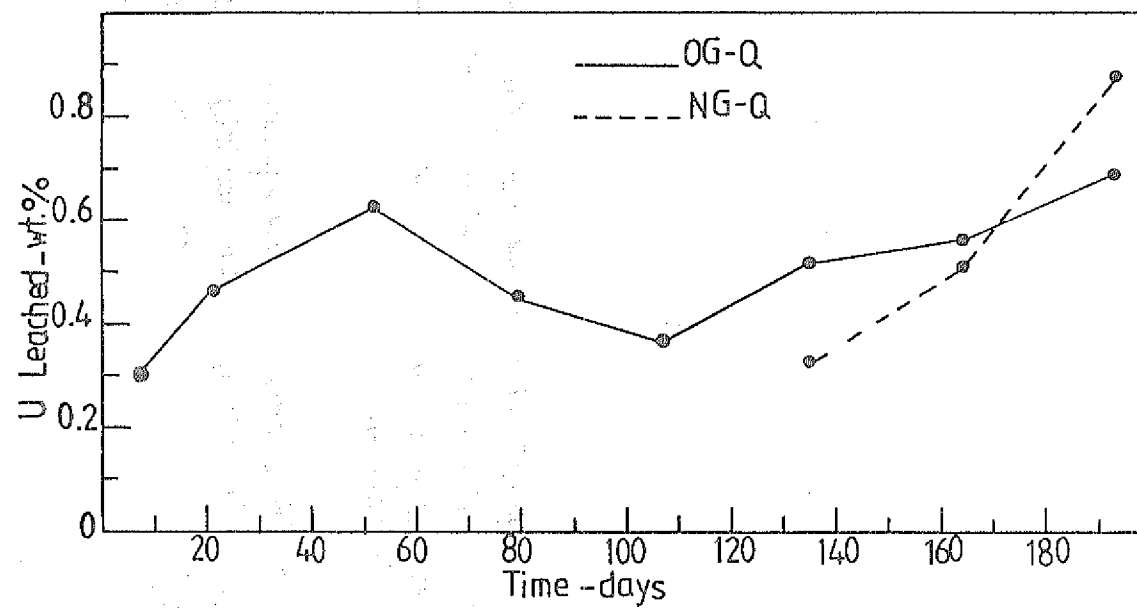


Figure 25: U fraction leached (wt.-%) from samples NG-Q and OG-Q in Q-brine at 50°C

6. CONCLUSIONS

The aluminosilicate binders (TROLIT geopolymers) investigated in this study are capable of forming strong monoliths with dried MAW. Waste loading should be below 50 wt.% of the reactive component. While other geopolymer additives do not participate in building the aluminosilicate network, they are quite important in achieving the high strength. Therefore, only 15 wt.% waste salt loading is possible when also high strength product is also required.

The microstructure of the products depends, not only on the composition of binders, but also on the waste to hardener ratio. In all cases, very small grains (in the order of a tenth of a micron) are formed. These are interconnected or bound together to form a monolith. Waste salts are dissolved or react in the hardener and incorporated in the matrix. No evidence of separate waste phases could be found.

Leach resistance of the products depends on the element being leached, the matrix composition, and the leach solution. In water, the kinetics of the process was relatively fast. Almost constant concentrations of leachate (Mo or Cs) were found after one week at room temperature. These constant values put leaching of Mo at 20 - 40 wt.% and Cs at 2-10 wt.%, based on the composition of the matrix. In Q-brine, there was a gradual increase in leachate concentrations (Sr, Cs, or Mo) from the start until almost 120 days. The rate became slow after that with leach fractions between 2 - 16 wt.% for Mo, 1-6 wt.% for Sr, and 4-26 wt.% for Cs, in about 120 days.

While the retention of Sr is good, Cs is fair, and Mo is poor. Considering the resemblance Tc, it is possible that ions with a high valence state are not incorporated in the matrix. This is also supported by the high leach rate of uranium. Ionic size also plays a role in the possibility of an ion being incorporated in the aluminosilicate cages.

The overall performance of cement-glass is relatively superior to the aluminosilicate binders investigated. Tolerance of Q-brine is far better. Also, leaching rates in Q-brine of Sr and Mo, and in water of Sr, Cs, and Mo are below those of aluminosilicates. In addition the Cs leach rate in water is better than most cements and some aluminosilicate binders.

Appendix A

Composition of simulated medium level waste solution. Nitrate salts were used for all elements.

Oxide	Concentration [g/l]
Na ₂ O	73.166
Al ₂ O ₃	0.435
CaO	2.099
Cr ₂ O ₃	0.117
Cs ₂ O	0.014
CuO	0.188
Fe ₂ O ₃	0.543
K ₂ O	0.096
MgO	1.244
MnO ₂	0.103
MoO ₃	0.57
NiO	0.102
RuO ₂	0.05
SrO	0.021
ZnO	0.187
ZrO ₂	0.108

NOMENCLATURE

MAW	Medium Activity Waste
ILW	Intermediate Level Waste (same as MAW)
LLW	Low Level Waste
TROLIT	Trademark of geopolymers produced by Hüls Troisdorf AG. TROLIT (AOS) produces foam-like material. TROLIT (AOM) produces condensed material. The latter is investigated in this study.
ROS & KOS	Reactive components of TROLIT analyses are given in Table 2
SECAR 51	High alumina cement ($\sim 51 \% \text{Al}_2\text{O}_3$)
PAW & PN	Sodium-silicate hardeners prepared from Portil-AW and Prottil-N respectively, (trademarks of Henkel KGaA Düsseldorf)
FABUTIT 748	Al_2PO_5 which is a hardener to the sodium silicates.
GP-(1 to 5)	MAW solidified with TROLIT with ROS as reactive component, and leached in water.
KP-(1 and 2)	MAW solidified with TROLIT with KOW as reactive component, and leached in water
S-(1 and 2)	MAW solidified with SECAR 51 and PAW, and leached in water.
MWO	Dry simulated MAW with composition as shown in Appendix A.
MWI	Denitrated MAW with excess formaldehyde.
MW2	Denitrated MAW with excess nitric acid.
B(G, K Or S)	Blank samples made of solidifying matrix without MAW for samples GP, KP, and S, respectively, and leached in water.
OG (H and Q)	U_3O_8 solidified with TROLIT and leached in water (H) or Q-brine (Q).
NG-(H and Q)	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solidified with TROLIT and leached in water (H) or Q-brine (Q).
NW-(H and Q)	$\text{MWO} + 0.04 \% \text{U}$ as $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solidified with TROLIT and leached in water (H) or Q-brine (Q).
TG-(H and Q)	$\text{MWO} + 0.3 \% \text{Tc}$ as NH_4TcO_4 solidified with TROLIT and leached in water (H) or Q-brine (Q).
(G, K, or S)Q	Samples of type GP, KP or S leached in Q-brine.

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