



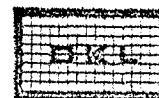
SOLIDIFICATION OF WASTES

"A review of the fundamentals of solidification, its history, recent developments and verification of its validity, uses and applications."

Prepared by:

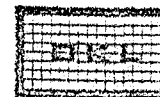
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by David Krofchak, P.Eng.

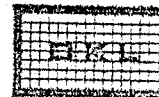
Solidification is the term which defines, in one word, the activity in which loose materials or liquids or sludges or combinations of these things "become solid" hard, firm or compact or are brought together in unity.

Everyone would agree that the earth's crust is formed of solid materials in general, notwithstanding the water in the lakes, seas and swamp areas. The soils are largely composed of silicate compounds. In fact, it has been estimated that up to 80% of the earth's surface or soils are composed of complex silicate compounds.

The importance of this is appreciated when it is realized that nearly all toxic pollutants originated from soils rich in various elements which, due to this, are defined as mineable ore! An ore rich in say copper is mined for its copper value, of course, and the copper in turn is converted into numerous copper compounds some of which invariably end up in wastes such as plating wastes. Applying this particular example to the Solidification Technology we would devise a way to convert the copper bearing wastes into a copper silicate compound, because in this form, the copper is insoluble in water and, therefore, non-toxic and a solid material not unlike a solid copper bearing soil or ore.

The complexity of solidification can be appreciated when one considers that to treat wastes into a form which can be solidified requires an extensive knowledge of chemistry. To take the treated wastes and convert them into typical silicate compounds analogous to soils requires a knowledge of geochemistry. To set up a practical process to carry out the steps to accomplish solidification requires a knowledge of chemical engineering and to tackle some of the huge problems of the world such as mine tailings requires the approach of civil engineering in order to execute the work in the realms of viable economics. All these disciplines must be recognized and used to make solidification of wastes a practical reality rather than a laboratory curiosity.

The history of solidification has to be traced back in retrospect by analogy to things that were done for specific purposes and, in fact, were not recognized as solidification in the context as outlined in this paper. For instance, the Romans found out that if they took lime, sand, stone and volcanic silica ash they could make concrete or synthetic stone. Modern concrete is Portland cement which is tri-calcium aluminum silicate. $(3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2)$. While this is a simplification of the formula it serves to illustrate that it is a silicate compound. Most of the earth's sedimentary rocks are complex mixtures of silicate compounds.



Typically silts formed sediments which, in turn, became clays, mud stones, shales, and sand stones. A cataloguing and analysis of all the different kinds of sedimentary rocks that exist on the earth in terms of the chemical structure would be an impossible task filling countless volumes of books and indeed whole libraries.

So what is the point of all this and what does it have to do with toxic wastes? Well, any combination of toxic wastes (excluding insoluble organics such as oil, gasoline and solvents) can be converted to sediments which, in turn, can be reacted into silicate compounds and become a solid material analogous to a soil or indeed a soil in its own right. Accomplishing this means that the waste is no longer a toxic substance to the environment.

This whole procedure is called solidification and has been patented. The title of the patent is "The Stepwise Treatment of Waste liquids, sludges and materials to form Solid Silicates". (Reference No. 1)

Silicate chemistry is a vast and infinite subject based on the silicon atom. It is remarkable that the elements, silicon and carbon, which resemble each other in so many respects, should play such different roles in living things.

Many mysteries exist in the world regarding explaining how certain large quartz crystals could have been formed when its virtual insolubility in water is appreciated and further, how was petrified wood (i.e. wood replaced by silica) formed? These and many other examples cannot as yet be duplicated in the laboratory. It would appear that nature has nailed down silicate chemistry in dramatic ways taken for granted in the world and here we are now struggling to invent ways to form wastes into silicate soils similar to that which nature has done very effectively with the elements over the millennia.

Based on this background, a major attack has been made on applying solidification to a large percentage of the liquid wastes hauled out of industries in Ontario. In 1976, a commercial sized pilot run and test was done in conjunction with and for the Ministry of Environment of Ontario. (See Reference No. 2)

This test was done on mixed wastes collected from all manner of industries. These tests were successful and resulted in a proposal being made to set up a large test site in Hamilton, Ontario. The site was completed in March 1977 and solidification of large volumes of wastes from all of the industries in Hamilton started in April. Over 350,000 gals. per month of wastes have been solidified since April, 1977. One month over 890,000 gallons was solidified.



The solidified material is used as soil cover for the garbage at the sanitary landfill site in Hamilton, Ontario, and at the present rate of "soil" production, it will take 25 years to cover the site.

In order to obtain an independent evaluation of this solidification application suitable for assisting in obtaining final approvals for the site and for other engineering and scientific reasons, a test program was designed by Dr. Bob McAndrew of the University of Toronto, Department of Metallurgy and Material Science. (See Reference No. 4) This work was carried out during the period of July – December, 1977. Over 25 leaching tests were conducted on 10 solidified product materials produced at the site and chemical analysis of over 90 liquid and solid samples requiring over 2,000 assay determination of individual elements were made. The conclusions from this test work were:

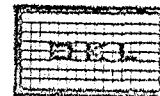
1. All samples gave similar results to each other with respect to low levels of leachability of toxic elements.
2. Total elements leaching out individually was generally less than 1 ppm.
3. The materials as solidified would meet all present environmental standards.
4. The solidified materials looked like typical soft brown clay/shales.

This is a major program which is still ongoing. The following descriptions and results were obtained from Dr. McAndrew's report.

The solidification process used in the test is proprietary and, therefore, only general process information is described. The solidification technology is covered by Canadian Patent No. 1024277 (issued 10th of January, 1978). Patents have been applied for in the U.S.A. and other countries. (Ref. No. 1 and No. 3).

In general, the test operation, consisted of the following steps:

1. Liquid waste received from various industrial sources by tank truck was unloaded into either of two 125,000 gallon holding lagoons. A third lagoon was used to blend 100,000 gallon lots of liquid waste prior to solidification treatment.
2. Solidification was done in 3,500 gallon batches. Alkaline and silicate reagents were added, in the required amounts, to the liquid waste in a blender and the resulting slurry was fed to the reaction tank.



3. When the mixing and initial solidification reaction was complete, the batch of solidified product was transferred by dump truck to a temporary storage pile for several days to allow initial curing prior to being moved in the final land fill site.
4. Each 100,000 gallon lagoon lot required 25 - 30 batches which were completed during a 3 - 4 day period. Liquid waste disposal required solidification of 2 - 4 lots per month during the summer of 1977.

Ten samples of solidified product were evaluated in the testing program. Seven were field samples of material produced at the Hamilton site while three additional samples were prepared in the laboratory. The stability of these product samples with respect to environmental attack by aqueous solutions was evaluated in a series of 25 leaching tests in the laboratory. These tests included both continuous flow leaching in glass columns, and constant volume leaching in stirred beakers and shaking flasks. The column leaching tests were run for 8 - 26 days while the constant volume leaching tests were run for 9 - 13 days.

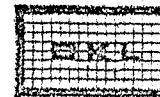
Chemical analyses were provided by Barringer Research Ltd., using a Multielement Radio Frequency Induction Coupled Plasma Emission Spectrometer.

Results

All samples tested gave similar results to each other in both the continuous flow column tests and in the constant volume shaking flash tests. Table 1 gives chemical analysis for a series of samples collected during a column test operated for 16 days at room temperature using tap water. The solidified product (3SP) was collected from the daily production at the Hamilton site on August 23rd, 1977.

Table 2 gives similar chemical analyses for shaking flask tests using the 3SP solidified field sample (Test 20b) plus two other solidified products prepared in the laboratory. The 11 SP laboratory material was produced using a sample of the original liquid waste (3LW) (Test 27b). The 10SP laboratory material was produced using the liquid waste (3LW) with higher concentrations of As, Cd, Co, Cu, Hg, Mo, Ni, Pb and Sb as shown for sample (3LWS) (Test 27a).

Also shown in Table 2 are the results from a shake flask test using a typical clay and soil mixture used for final cover on the land fill site. The results are essentially the same for the clay and soil mixture as they are for the solidified product material.



Discussion

The following general observations were made:

1. The concentration of individual heavy metals was generally less than 1 ppm and reached constant equilibrium or steady state values within several days. These elements include Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti, V and Zn.
2. The steady state values were slightly different for different tests depending on the sample origin, column bed depth and bed permeability. The column bed depths were in the 10 – 20 cm range and bed permeabilities were found to be in the range $2 - 6 \times 10^{-5}$ cm/sec. which is also typical for nature soils.
3. The concentration of other elements also reached constant values which were generally less than 1 ppm. These elements include Al, B, Ba, Mg, and P. All solutions contained Ca in the range 600 – 1,000 ppm which is typical for calcium saturation.
4. Alkali metals originally present in the waste liquids leached out relatively quickly (1 – 2 weeks) from the solidified product. Thereafter, the alkali metal concentrations remain constant and equal to the concentration of the water used in the column leaching tests (i. e. 20 – 25 ppm Na₃ 2.3 ppm K).
5. Based on measured bed permeability and steady state equilibrium concentrations estimates can be made of the time required for complete dissolution of each element. For example, using an average annual rainfall of 80 cm/year, the time for complete dissolution per centimetre of bed height would be:

| | | |
|------|----|--------------|
| e.g. | Zn | 20,000 years |
| | Cd | 140 years |
| | Ca | 2.1 years |

The actual chemistry by which the metal impurities are tied up by solidification is complex and probably involves the formation of some or all of the following: hydroxides, sulphates, carbonates, and silicates as well as other compounds. In their initial form, these precipitates, like all precipitates, are in their least stable or most soluble form. These active forms tend to convert to more stable forms through internal structural reordering. Aging or curing therefore should result in more stable and less soluble precipitated material.

Studies are continuing with the objective of defining, in more detail, the chemical and physical structure of the final solidified product material. The methods being used include x-ray diffraction, scanning electron microscopy with an X-ray fluorescence probe, thermal gravimetric analysis and differential thermal analysis.

TABLE 1 - RESULTS OF COLUMN LEACH

| Time, days Sample, mls pH | Solidified Product 3Sp | LEACHATE SAMPLES | | | | | | Tap Water |
|---------------------------------|------------------------------|-------------------|-------------------|-------------------|---------------------|--------------------|-------|--------------|
| | | 3CL2 | 3CL3 | 3CL4 | 3CL7 | 3CL10 | | |
| | | 0-5 150 8.4 | 5-7 78 10.8 | 7-9 31 10.2 | 12-13 36 10.5 | 15-16 35 --- | 7.3 | |
| Assay, ppm | | | | | | | | |
| 1. Aluminum (Al) | 27400 | .3 | .6 | .2 | .2 | .2 | .04 | |
| 2. Arsenic (As) | --- | --- | --- | --- | --- | --- | --- | |
| 3. Barium (Ba) | 170 | .3 | .1 | <.08 | <.08 | <.08 | <.02 | |
| 4. Boron (B) | --- | 1.0 | .8 | .4 | .3 | .2 | .95 | |
| 5. Cadmium (Cd) | 118 | <.1 | <.1 | .1 | .1 | .1 | <.1 | |
| 6. Calcium (Ca) | 165000 | 900 | 580 | 570 | 630 | 630 | .56 | |
| 7. Chromium (Cr) | 880 | .22 | .09 | .05 | .01 | <.01 | <.01 | |
| 8. Cobalt (Co) | 26 | <.02 | <.02 | .02 | .02 | .02 | .16 | |
| 9. Copper (Cu) | 61 | .33 | .14 | .11 | .05 | .05 | .03 | |
| 10. Iron (Fe) | 52600 | .02 | .08 | .02 | .04 | .01 | <.005 | |
| 11. Lead (Pb) | --- | <.5 | <.5 | <.5 | <.5 | <.5 | --- | |
| 12. Magnesium (Mg) | 8400 | .47 | .34 | .36 | .05 | .02 | 3.4 | |
| 13. Manganese (Mn) | 750 | <.001 | <.001 | <.09 | <.04 | <.08 | .07 | |
| 14. Mercury (Hg) | --- | --- | --- | --- | --- | --- | --- | |
| 15. Molybdenum (Mo) | --- | 1.60 | .78 | .59 | .05 | .02 | .13 | |
| 16. Nickel (Ni) | 144 | <.1 | <.1 | <.1 | <.1 | <.1 | <.02 | |
| 17. Phosphorous (P) | 1120 | <.5 | .5 | .8 | .8 | .9 | <.1 | |
| 18. Potassium (K) | --- | 4 | 3 | 2 | 2 | 2 | 2 | |
| 19. Sodium (Na) | 7600 | 1280 | 68 | 41 | 25 | 22 | 22 | |
| 20. Silicon (Si) | 183000 | 4.5 | 4.5 | 2.8 | 1.8 | 1.6 | .56 | |
| 21. Strontium (Sr) | 190 | 1.2 | .87 | .73 | .87 | .90 | .19 | |
| 22. Titanium (Ti) | 1810 | .001 | .001 | .004 | .006 | .005 | .002 | |
| 23. Vanadium (V) | 52 | <.01 | <.01 | <.01 | <.01 | <.01 | .02 | |
| 24. Zinc (Zn) | 42800 | <.01 | <.01 | <.01 | <.01 | <.01 | <.01 | |

TABLE 2 - COMPARISON OF SHAKE FLASK TESTS

| Charge Wt, g Water, ml Time, days Final pH | Liquid Waste 3LW | Doped Waste 3LWS | Tap Water | Field 3SP Filtrate 3FL | Lab 11 SP Filtrate 11FL | Doped 1OSP Filtrate 1OFL | Clay Leach | |
|-----------------------------------------------------|---------------------|---------------------|--------------|------------------------------|-------------------------------|--------------------------------|---------------|-------------------|
| | | | | | | | Clay 3 CLY | Filtrate 3 CLY |
| 1. Aluminum (Al) | 32 | 50 | .04 | <.1 | .4 | .6 | 60000 | <.1 |
| 2. Arsenic (As) | -- | 28 | -- | -- | -- | .02 | -- | -- |
| 3. Barium (Ba) | 0.2 | 314 | <.02 | .08 | <.05 | <.05 | 410 | <.08 |
| 4. Boron (B) | -- | 46 | .95 | .14 | .08 | .10 | -- | .30 |
| 5. Cadmium (Cd) | 23 | 228 | <.1 | <.1 | <.1 | <.1 | <.1 | <.1 |
| 6. Calcium (Ca) | 672 | 514 | .56 | 880 | 2620 | 2790 | 110000 | 137 |
| 7. Chromium (Cr) | 1740 | 1480 | <.01 | <.01 | <.01 | <.01 | <.01 | <.01 |
| 8. Cobalt (Co) | 3.5 | 193 | .16 | .02 | .06 | .16 | 13.7 | .19 |
| 9. Copper (Cu) | 12 | 224 | .03 | .27 | .52 | .67 | 30.2 | .05 |
| 10. Iron (Fe) | 22200 | 19500 | <.005 | <.005 | <.005 | <.005 | 29000 | <.005 |
| 11. Lead (Pb) | <.1 | 9 | -- | .3 | .26 | .26 | <.2 | .3 |
| 12. Magnesium (Mg) | 90 | 135 | 13.4 | .9 | <.001 | <.001 | 10300 | 16 |
| 13. Manganese (Mn) | 277 | 161 | .07 | <.001 | <.001 | .001 | 727 | .13 |
| 14. Mercury (Hg) | -- | 152 | -- | -- | -- | <.0003 | -- | -- |
| 15. Molybdenum (Mo) | .71 | 270 | .13 | .96 | .86 | .36 | <.02 | .18 |
| 16. Nickel (Ni) | 83 | 217 | <.02 | <.1 | .2 | <.1 | 24 | <.1 |
| 17. Phosphorous (P) | 171 | 136 | <.1 | <.1 | <.1 | <.1 | 490 | .9 |
| 18. Potassium (K) | 41 | 9 | 2 | -- | 41 | 27 | -- | -- |
| 19. Sodium (Na) | 923 | 2720 | 22 | 1140 | 3750 | 1350 | 8500 | 36 |
| 20. Silicon (Si) | 30.2 | 47.4 | .56 | .91 | .83 | 1.2 | -- | 6.5 |
| 21. Strontium (Sr) | 2.5 | 3.9 | .19 | 1.4 | 3.5 | 5.0 | 246 | .23 |
| 22. Titanium (Ti) | 3.4 | 4.3 | .002 | <.001 | .03 | .04 | 3290 | .01 |
| 23. Vanadium (V) | 2.3 | .76 | .02 | <.01 | <.01 | <.01 | 87 | .02 |
| 24. Zinc (Zn) | 28100 | 15900 | <.01 | <.01 | 1 | 1 | <.01 | <.01 |

We maintain a 6,000 sq. ft. laboratory and sample library for solidification and it is run by a qualified geochemist. Virtually every day, some sample of waste from the North American Continent is solidified along with other ongoing test programs.

As the enormous size of the subject of solidification has unfolded, searching questions have understandably arisen. One of which has been the very nature of the silicate and other compounds linking the particles together. To this end, we have commissioned the Eitel Institute of Silicate Science through its director, Professor William Kneller, Ph. D. to conduct in-depth studies aided by Electron Microscopy and X-Ray Diffraction methods on specific solidified samples. To date the tests shown on these samples studied, that the compounds formed by the solidification process are, in fact, silicate compounds. Work is proceeding to identify the specific silicate compounds in various samples.

The following shows an example of an electron microscope study of a sample of uranium mine tailings before and after solidification and you will note the definite well formed crystal growth shown in the solidified sample.

The analyses of the cementitious material illustrated in the text show a compound similar to that of hydrogarnet or hydrogrossular ($\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_8(\text{SiO}_4)_{1-m}(\text{OH})_{4m}$). Other compounds which may be present, but have not been confirmed, are similar compositionally to gehlenite or hardystonite, both of which are silicate compounds.

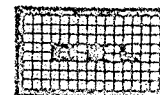


Photo No. 1
Untreated Tailings of Denison Mines
Secondary Filter Cake

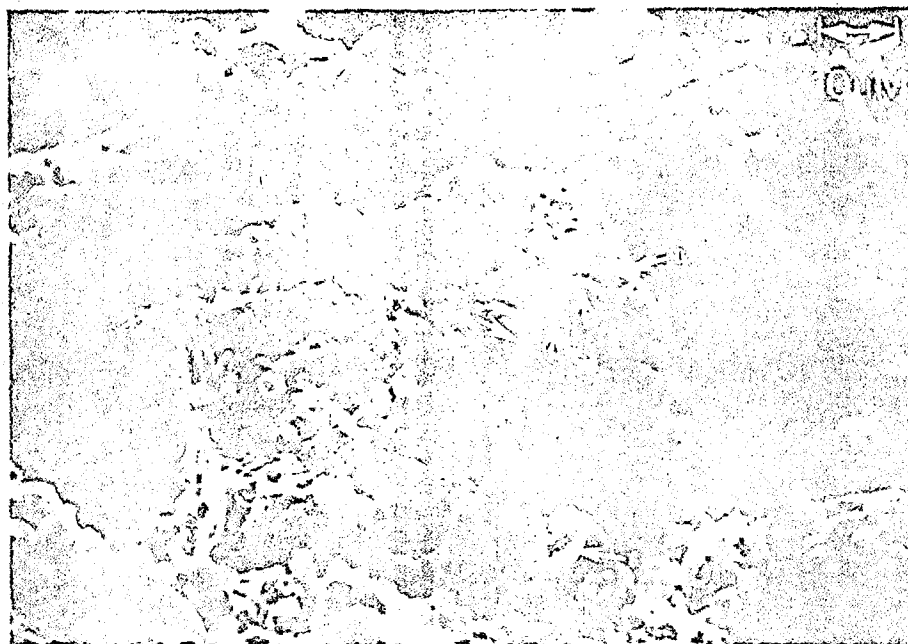


Photo No. 2
Solidified Denison Mines Tailings
Secondary Filter Cake

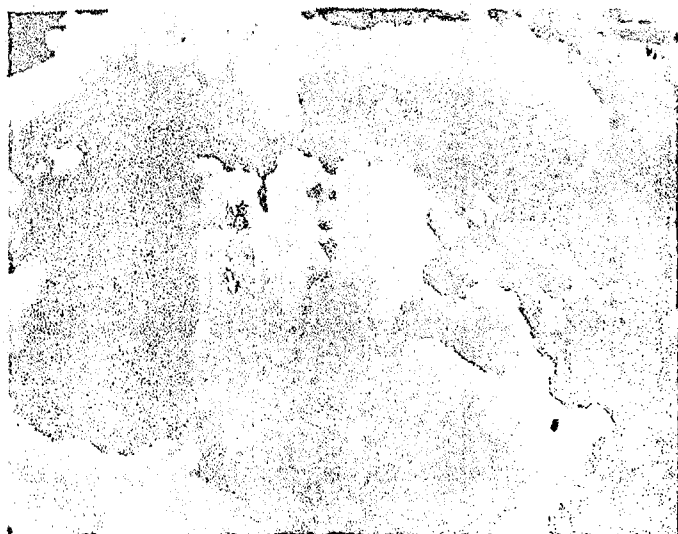
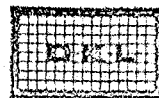


Photo No. 3

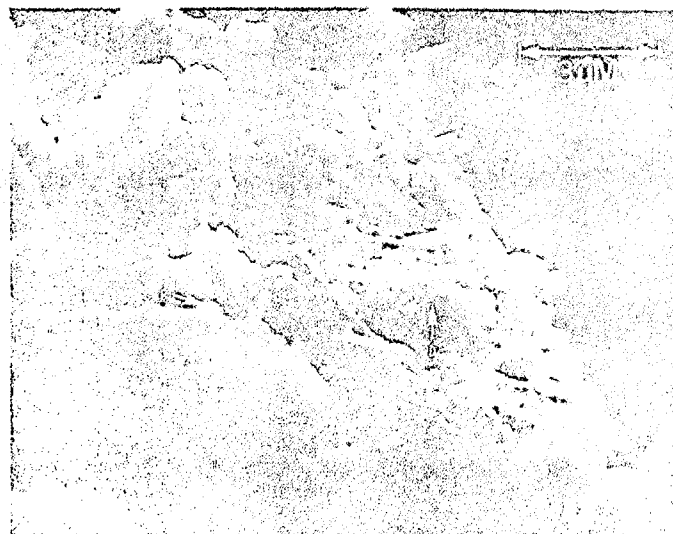


Photo No. 4

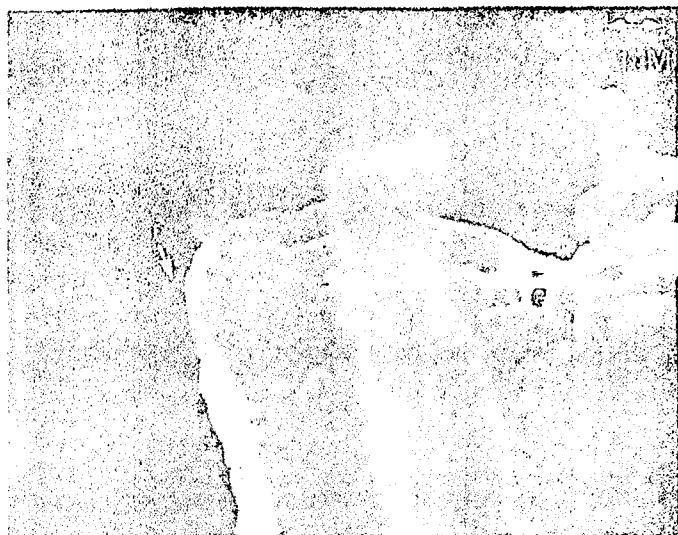


Photo No. 5

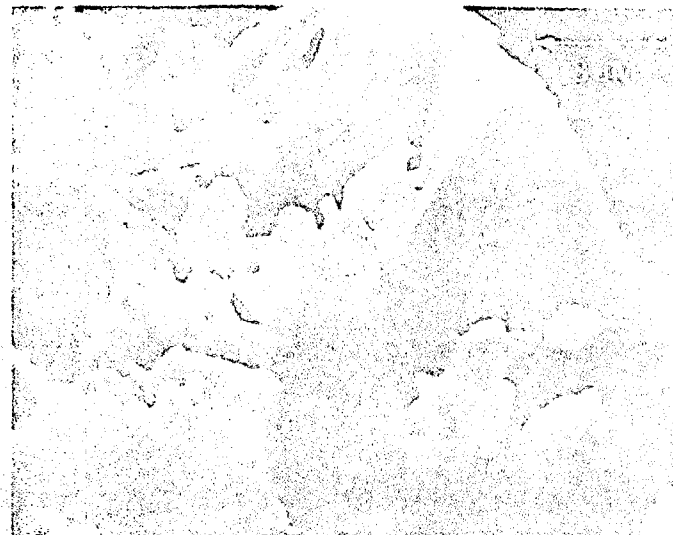


Photo No. 6

Photos No. 3, No. 4, No. 5 and No. 6 are close-ups of the points A, B, C, D, E, and F marked by the arrows on photo No. 2.

In comparing photo No. 1 with No. 2, it will be at once observed that the unsolidified tailings show as clearly defined broken rock fragments and crystals.

Photo No. 2, the solidified tailings, has numerous growths on and between the crystals and rock fragments. On some of the new material observed, we marked the points A, B, C, D, E and F and called for the electron microscope to zero in on these points as shown in photos 3, 4, 5 and 6, and take a dispersive x-ray analysis of the new material at these 5 points. The purpose of this being to determine the composition of the new material that has been formed and is holding the tailings together as a sedimentary rock.

The analysis of points A, B, C, D, E and F are tabulated as follows:

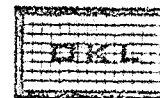
| Point | Na% | Mg% | Al% | Si% | S% | K% | Ca% | Fe% |
|-------|------|------|------|-------|-------|------|-------|------|
| A | 2.09 | 0.17 | 0.25 | 2.43 | 19.98 | 0.19 | 28.39 | 0.45 |
| B | 1.33 | 1.09 | 0.49 | 9.13 | 3.63 | 0.30 | 37.22 | 0.78 |
| C | 1.91 | 0.65 | 0.59 | 5.12 | 17.93 | 0.16 | 26.63 | 0.99 |
| D | 2.21 | 0.40 | 2.31 | 46.77 | 0.12 | 0.06 | 1.23 | 0.86 |
| E | 1.31 | 1.60 | 2.38 | 36.68 | 1.89 | 1.11 | 7.38 | 1.58 |
| F | 1.65 | 3.16 | 5.86 | 23.85 | 3.27 | 4.57 | 8.07 | 3.54 |

At this stage in Dr. Knellers research indications are that the silicates present in the cement are an admixture of sulphates, aluminates, sulpha-aluminates and silicates. The particles located at Points A and C are most probably calcium sulphate with other minor chemical phases being present. Points D, E and F appear to be silica rich. Point D might be a partially crystallized silica gel, whereas Points E and F might be true complex silicate compounds.

As further evidence of the validity of the above results, we have taken samples of the solidified tailings and immersed them in water for prolonged periods of time (several months) and they did not collapse or fall apart as would be the case if the Na, Mg, SO₄ and K was not tied up as an insoluble silicate.

If the unsolidified tailings are dried, they become hard but on immediate contact with water, they collapse into a flowable mud, sludge or slime and this happens regardless of how often this is done. Thus, these tailings, untreated, are never stable.

In the case of mixed hazardous wastes containing all kinds of metals in solution such as Cu, Cr, Ni, Cd, and Fe, etc., these metals are first precipitated and the resultant sludge is reacted with an active silicate to form the mass into a solid silicate as a complex metallic silicate.



Applications of Solidification:

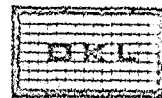
The technology of solidification is a very large subject spanning most major industrial endeavours. Of particular importance are:

1. Industrial Wastes such as sludge, dusts and other materials.
2. Mining Wastes such as the problems of tailings disposal and all manner of other wastes associated with mining and the backfilling of mines.
3. Civil Engineering applications such as dredging, land reclamation and stabilization of soils and earth dams, etc.
4. Municipal Sewage such as the disposal of sewage sludge and the improvement of sewage treatment plant techniques.
5. Special Applications: There are numerous world scale problems which because of their size and complexities require separate categorization. Some examples of these are:
 - The Great Canadian Athabasca Tar Sands
 - The Florida Phosphate Mines which produce 30% of the world's phosphate fertilizers.
 - Coal mining produces large quantities of coal dust which, when solidified, could become saleable coal.
 - Large industrial in-house wastes have to be dealt with by specially designed schemes and programs utilizing various wastes available to reduce the cost of total pollution control and produce a useful end material such as high grade land fill, road sub-base, or in the case of steel mills, a possible feed for blast furnaces.

It is expected that solidification based on silicate chemistry will find a growing and permanent place in the array of modern technology as applied to not only environmental problems but to many commercially important items such as mine backfill, recovery of coal dust and production of road base, etc.

Conclusions

The work-to-date on the solidification of wastes based on a stepwise treatment of wastes to form solid silicates has proven itself both in the laboratory and on full scale applications in the field. It is now known that the various steps to accomplish this vary for each mixture of wastes — once the formulation has been determined and a solid silicate matrix or compound formed, the final material resembles a typical soil such as soft fine grained shale, mudstone or sandstone.



An interesting aspect of this work is that while, for years, we have worked at solidifying various wastes and considered it a solution to that particular waste problem, and it is only recently that it was realized that the solidification technique and processes were, in fact, a way of accelerating geochemical processes which have taken centuries to accomplish the same thing. e.g. the formation of the sedimentary rocks.

In other words, since the constituents of most wastes originated from the earth in rocks, mostly associated with silicates, we have reformed the wastes back into a silicate soil in the form of a silicate sedimentary rock. This being the case, there can be no doubt as to solidification being a permanent and ultimate solution to many hazardous waste problems.

References

- No. 1 Canadian Patent No. 1024277 entitled "The Stepwise Treatment of Aqueous Wastes to Form Solid Silicates", Inventor David Krofchak. Issued 78.01.10.
- No. 2 An Assessment of a Process for the Solidification and Stabilization of Liquid Industrial Wastes. 1976 by the Ontario Ministry of the Environment, Industrial Section, Pollution Control Branch.
- No. 3 Patents have been filed in most foreign countries including the U.S.A. As of this date, the patent has been granted and issued in Canada (see Ref. No. 1) and just recently, in the U.S.A. The Patent in the U.S.A. was allowed on April 10th, 1978.
- No. 4 Preliminary Report on the Technical Assessment of a Solidification Process for Treating Industrial Liquid Wastes by R. T. McAndrew, Ph.D., P.Eng., Jan. 1978