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# U.S.S.R. POLYMER CONCRETES—LABORATORY TESTS OF BINDERS

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16. ABSTRACT
Bureau of Reclamation has been involved with the Soviet Union in a scientific exchange program on polymer concrete since 1974. The program included an exchange of materials used by each country; in 1980, samples of the U.S.S.R. polymer materials were received. Bureau interest focused on a family of binders for polymer concrete that are manufactured from agricultural byproducts — a group of furan materials. A chemical analysis was made of the materials; and several specimens were made and tested for various properties such as compressive strength, modulus of elasticity, and Poisson's ratio, as well as various tensile and flexural properties.

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# U.S.S.R. Polymer Concretes — Laboratory Tests of Binders

by
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Concrete and Structural Branch
Division of Research
Engineering and Research Center
Denver, Colorado

November 1983

SI METRIC

UNITED STATES DEPARTMENT OF THE INTERIOR ★ BUREAU OF RECLAMATION

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. Administration.

**The research covered by this report was funded under the Bureau of Reclamation Program Related Engineering and Scientific Studies allocation Research Project No. DR-256 *Engineering Materials.***

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# INTRODUCTION

This report covers a joint study performed as part of a **U.S./U.S.S.R. Joint Working Group on Plastic Films and Soil Stabilizers** in the field of *Plastics in Hydrotechnical Construction* (U.S. State Dept. Project No. 01.120401 – U.S.S.R. Project Categories II-3-1 and II-3-2). This was done under the U.S./U.S.S.R. Working Group program for **Water Resources** under the Soviet-American Joint Commission on *Scientific and Technical Cooperation Program.* The report covers essentially the work done in the period 1975-82. The joint study was made possible by the U.S./U.S.S.R. *Agreement on Cooperation in the Fields of Science and Technology,* first signed in 1972.

The U.S. Polymer Team was composed of John Scanlon, Corps of Engineers, Waterways Experiment Station (team leader); Carl Selander, Bureau of Reclamation (now retired); and representatives from the U.S. Air Force, National Bureau of Standards, and private industry.

The U.S. Polymer Concrete Team made several trips to the U.S.S.R. (1977-79). Scientific research institutes and several water resources development projects were visited. They were:

- Scientific Research Center of the Hydroproject Institute, Moscow
- MISI (Moscow Institute of Civil Engineering), Moscow
- NIIZhB (Gosstroy Scientific Institute of Reinforced Concrete), Moscow
- UkrNIIGiM (Ukrainian Scientific Research Institute of Hydraulic Engineering and Reclamation), Kiev
- SANIIRI (Central Asian Scientific Research Institute of Irrigation), Tashkent
- Charvasksky Hydroelectric Complex, Tashkent
- Hydroelectric Power Station, Siberia
- Kakhovka Irrigation Canal System near the Black Sea

The Soviet Polymer Concrete Team was composed of Dr. P. I. Kovalenko — team leader — UkrNIIGiM; Professor V. V. Paturoev, NIIZhB; L. A. Igonin, Hydroproject Institute; Sh. M. Makhmuldov, SANIIRI; plus many representatives from these and other scientific and engineering organizations. The Soviet team visited the United States three times (1977-79). These visits were to:

- Bureau of Reclamation — E&R Center, Denver, Colorado,

- Corps of Engineers — Waterways Experiment Station, Vicksburg, Mississippi,
- Brookhaven National Laboratory, Upton, New York,
- Federal Highway Administration — Fairbanks Laboratory — near Washington, D.C.,

and several construction projects and industries involved with polymer concrete applications.

An exchange of materials used in each country was part of the program. Materials of common interest were identified during team visits; in 1980, particular samples were exchanged. The U.S. interest focused on a family of binders for polymer concretes that are manufactured from agricultural by-products — a group of furan materials. The Soviet interest centered on polymer concretes made from organic binders of petroleum origin as well as on other polymer modifiers and additives.

The term *polymer concretes* is used sometimes rather loosely to refer to a number of different types of concrete materials containing polymers. In a narrower and more proper sense, *polymer concretes* refer to a type of concrete material consisting of aggregate and a polymer binder. In the Soviet Union, polymer concretes (or P-concretes) is used in a broad sense to refer to a broad group of materials that includes:

1. PC (polymer concrete),
2. PIC (polymer impregnated concrete),
3. Polymer portland cement concrete,
4. PSC (polymer silicate concrete), and
5. Several other materials ordinarily not considered as polymer concretes in the United States.

Figure 1 is a diagram of Soviet classification P-concretes. In the United States, the closest term to P-concretes is *concrete polymer materials* that include only polymer concrete, polymer impregnated concrete, and polymer portland cement concrete.

## CONCLUSIONS

The following are conclusions from testing several U.S.S.R. P-concretes:

1. Test results of FA PC (furfural acetone polymer concrete) are questionable, as the test specimens did not appear to be of good quality. The specimens tested showed low compressive strength (11 to 12 MPa). A refinement of materials and mix-cure procedures could produce FA PC having compressive strengths in the range of 25 to 40 MPa. Specimens of FA PC showed good durability in freezing and thawing resistance (2050 cycles), and good acid resistance (12 months) and no loss of compressive strength.

2. Furfural acetone epoxy polymer concrete showed good compressive strength (100 MPa), good freezing and thawing resistance (2050 cycles), and no loss of compressive strength. In 5 percent sulfuric acid, specimens swelled and split because portland cement filler reacted with the acid.

3. Polymer silicate concrete showed a compressive strength of 23 to 25 MPa and showed good acid resistance (5 percent sulfuric acid for 12 months) and no loss of compressive strength. Specimens of polymer silicate PC failed the freezing and thawing tests — having a mass loss of 27 percent in less than 1450 cycles.

4. Polymer-impregnated concrete showed good compressive properties having a compressive strength of 125 MPa. Since this compares well with Bureau and Brookhaven National Laboratories work with MMA (methyl methacrylate) PIC, it appears that U.S.S.R. PIC would have good durability and mechanical properties.

## ANALYSIS OF U.S.S.R. MATERIALS

According to the U.S./U.S.S.R. Working Group program, the Soviets sent the U.S. component materials samples for making several kinds of polymer concretes and related materials. Preliminary analysis was made on some U.S.S.R. sample materials to confirm their composition and to provide information on the materials' purity. It is noted that furan resins should not be expected to be refined materials designed to produce products with superior properties. It is likely that emphasis has been given to use of relatively unrefined materials (which are essentially agricultural by-products) and that these materials have been developed into low-cost products for acceptable rather than for superior properties.

## Furfuryl Alcohol

*Furfuryl alcohol assay*

| Material | Percent |
|---|---|
| Furfuryl alcohol | 96 |
| Furfural | 0.6 |
| Tetrahydrofurfuryl alcohol | 0.3 |
| Methylfurfuryl alcohol | 0.6 |
| Water | 0.3 |
| Unknown No. 1 | 0.3 |
| Unknown No. 2 | 0.7 |
| Trace of higher molecular weight material | |

This assay indicates Soviet furfuryl alcohol is somewhat less pure than commercially available furfuryl alcohol in the United States. Furfuryl alcohol is available commercially in the United States; it meets or exceeds an assay of 98 percent FA, a maximum of 0.7 percent furfural, and a maximum of 0.3 percent moisture.

## Furfural Acetone Resin

*DFA and MFA in furfural acetone*

| Material | Percent |
|---|---|
| MFA (monofurfurlidene acetone) | 16 |
| DFA (difurfurlidene acetone) | 23 to 28 |
| 5-methylfurfural | 2 |
| Furfural | 25 to 26 |
| Acetone | 0.3 |
| Water | 5.8 |
| Ash | 0.333 |
| Iron | 0.144 |
| High molecular weight impurity | 11 |

Note: 2FA and 3FA are U.S.S.R. designations that refer to the starting ratio of furfural to acetone used to make the particular resin.

The proportion of DFA and MFA in the U.S.S.R. furfural acetone is of interest as it reflects the starting molar ratios of furfural and acetone in the condensative reaction to produce the FA resin. The amount of DFA and MFA also has an effect on the final properties of the FA PC. The above assay indicates that this FA resin is not a refined product, but would likely be a 2FA or 3FA resin in the U.S.S.R. Furfural acetone resin should have a good balance of properties in regards to polymerization rate, unwanted reaction by-products, and final properties of the end product. The effect of furfural in the resin on the properties of the final product has not been fully investigated; but it probably has an adverse effect. It is noted that furfural is regarded as a toxic material.

**FAED (furfural acetone epoxy resin)**

*Furfural acetone epoxy resin assay*

| Material | Percent* |
|---|---|
| MFA (monofurfurlidene acetone) | 40 |
| DFA (difurfurlidene acetone) | 26 to 27 |
| 5-methylfurfural | n.d. |
| Furfural | trace, < 0.3 |
| Acetone | n.d. |
| Water | < 0.5 |
| Ash | 0.198 |
| Iron | 0.001 |
| Bisphenol A diglycidyl ether resin | 29 |

* n.d. not detected

Bisphenol A diglycidyl ether is a typical epoxy resin. The assay indicates that FAED resin probably corresponds to FAED-30 in Soviet terminology. This particular FAED resin was prepared with an FA resin of higher purity and a little different composition than the analyzed sample of FA. The FA in the FAED resin appears to have been prepared with starting materials of a lower *furfural to acetone* molar ratio than the analyzed FA sample, possibly in Soviet terminology an FA or FAM (modified furfural acetone) resin.

**PEPA (polyethylene polyamine)**

The PEPA curing agent appears to be triethylenetetramine (possibly a mixture of homologues).

## U.S.S.R. P-CONCRETES EVALUATED

The Soviet approach to the development of polymer concrete for applications to hydraulic structures was to use agricultural by-products for hydraulic structure applications. Their work included:

- the use of epoxies and epoxy mortar, which is similar to the work done in the United States and elsewhere,
- the development and use of modified furan resins for polymer concrete applications, which — until recently — have not been given much attention in the United States, and
- the use of several other specialty products.

Materials tested at the Bureau of Reclamation include:

1. Furfural Acetone Polymer Concrete (FA PC)
2. Furfural Acetone — Epoxy Polymer Concrete (FAED PC)
3. Polymer Silicate Concrete
4. Polymer Impregnated Concrete (PIC)

**Furfural Acetone Polymer Concrete**

The FA PC was prepared using Soviet resin and curing agent with Bureau aggregate (table 1). Specimens were prepared by the following steps:

1. Mix sand from 2 to 3 minutes
2. Add FA, and mix from 2 to 3 minutes
3. Add BSA (benzene sulfonic acid), and mix from 2 to 3 minutes
4. Cast specimens and cure them in molds at room temperature (20 °C ± 5 °C) for 1 day
5. Heat cure in molds at 80 °C for 10 hours
6. Before stripping, cool in molds for 24 hours

The quality of the prepared FA PC specimens was not as good as expected, and test results should not be considered to be representative of what can be expected from good quality FA PC. The FA PC specimens expanded about 2 percent upon curing, and when stripped from the molds the specimens had a charred or burned appearance. It appeared that the specimens may have overheated during curing.

Compressive and flexural tests showed lower strength than expected, but double shear and durability properties appeared good. Table 2 shows a summary of the data. After 2050 cycles in freezing and thawing, and 12 months in 5 percent sulfuric acid, compressive strengths were 12 MPa as compared to 11 MPa for unexposed specimens. The data indicate that FA PC has good freeze-thaw and acid resistance.

### Furfural Acetone Epoxy Polymer Concrete

Specimens of FAED PC were batched using Bureau fine aggregate, portland cement as a filler, and U.S.S.R. resin and curing agents (table 1). Specimens were prepared by the following steps:

1. Mix sand and cement for 3 minutes
2. Add FAED (furfural acetone epoxy), and mix 3 minutes
3. Add PEPA (polyethylene polyamine), and mix 3 minutes
4. Cast specimens in molds and cure at room temperature (20 °C ± 5 °C) for 1 day
5. Heat cure in molds at 90 °C for 10 hours
6. Before stripping, cool in molds for 24 hours

Materials were mixed, cast, and cured without problems. Compressive strength for FAED PC was 100 MPa, which is about three times that of conventional portland cement concrete. The FAED PC showed good durability in freezing and thawing; after 2050 cycles, the compressive strength was still 100 MPa. However, in 5 percent sulfuric acid, the portland cement filler reacted with the acid and caused the specimens to swell and split as shown on figure 2. Test results are shown in table 2.

### Polymer Silicate Concrete

Specimens of PSC (polymer silicate concrete) were prepared using Bureau aggregate; other constituents were furnished by the Soviet Union. Proportions are shown in table 1. Specimens were prepared by the following steps:

1. Mix sand, gravel, andesite, and sodium fluosilicate for 3 minutes
2. Mix in water glass for 2 minutes

3. Mix in furfuryl alcohol for 2 minutes
4. Cure 1 day at room temperature
5. Heat cure at 90 °C for 10 hours
6. Before stripping, cool in molds 24 hours

The PSC specimens had a compressive strength of 25 MPa. The specimens showed good acid resistance in 5 percent sulfuric acid and no loss of compressive strength. However, the specimens failed in freezing and thawing and showed over 27 percent mass loss in less than 1450 cycles. The test data summary is shown in table 2.

**Polymer Impregnated Concrete**

Conventional concrete of 75- by 150-mm cylindrical specimens were prepared with Bureau materials. The concrete cylinders were impregnated with U.S.S.R. methyl methacrylate according to a procedure provided by the Soviets. The process was:

1. Dry concrete specimens overnight at 143 to 150 °C
2. Cool specimens at about 30 °C for several (6) hours
3. Catalyze U.S.S.R. MMA (methyl methacrylate) with U.S.S.R. benzoyl peroxide (3 percent by mass of MMA)
4. Place specimens under vacuum at 585 mm Hg for 1 hour
5. Immerse and soak specimens at atmospheric pressure for 2-1/2 hours
6. Polymerize MMA-impregnated specimens under water overnight at 74 to 76 °C

Tests showed these specimens to have good compressive strength — averaging 125 MPa. Test data are in table 3. Since only a limited amount of U.S.S.R. MMA was available, only two cylinders were impregnated. Results appear similar to MMA PIC tested in Bureau work[1] which showed good durability and mechanical properties.

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[1] G. W. DePuy, Rep. GR-4-75, *Process Technology Developments with Concrete-Polymer Materials,* U.S. Dept. of the Interior, Bureau of Reclamation, 63 p., Denver, Colorado, June 1975.

## Table 1. — *Polymer concrete mixes (U.S.S.R.)*

### FA Polymer concrete mix

***Aggregate system***

| Aggregate sieve size, mm | Amount, g |
|---|---|
| 4.75 to 9.5 | 11 860 |
| 2.36 to 4.75 | 8 590 |
| 1.18 to 2.36 | 6 470 |
| 0.60 to 1.18 | 4 290 |
| 0.30 to 0.60 | 2 880 |
| 0.15 to 0.30 | 1 790 |
| Pan | 9 100 |
| Total | 44 980 |

***Resin system***

| Material | Amount, g |
|---|---|
| [1]FA | 5180 |
| [2]BSA | 1270 |

*Mix directions*

1. Mix sand 2 to 3 minutes
2. Mix in FA
3. Mix in BAS
4. Cure in molds at room temperature 1 day
5. Heat cure in molds at 80 °C for 10 hours
6. Before stripping, cool in molds 24 hours

### [3]FAED [4]PC mix

***Aggregate system***

| Aggregate sieve size, mm | Amount, g |
|---|---|
| 4.75 to 9.5 | 7 894.9 |
| 2.36 to 4.75 | 5 807.2 |
| 1.18 to 2.36 | 4 355.4 |
| 0.60 to 1.18 | 2 907.6 |
| 0.30 to 0.60 | 1 950.9 |
| 0.15 to 0.30 | 1 225.0 |
| Portland cement | 6 079.4 |
| Total | 30 306.4 |

***Resin system***

| Material | Amount, g |
|---|---|
| [3]FAED | 3742.9 |
| [4]PEPA | 714.6 |

*Mix directions*

1. Mix sand and cement 3 minutes
2. Mix in FAED
3. Mix in PEPA
4. Cure in molds at room temperature 1 day
5. Heat cure in molds at 90 °C for 10 hours
6. Before stripping, cool in molds 24 hours

## Table 1. — *Polymer concrete mixes (U.S.S.R.)* – Continued

**Polymer silicate concrete mix**

*Mix system*

| Aggregate sieve size, mm | Amount, g |
|---|---|
| 9.5 to 19.0 | 8 438.6 |
| 4.75 to 9.5 | 8 438.6 |
| 2.36 to 4.75 | 3 130.5 |
| 1.18 to 2.36 | 3 130.5 |
| Andesite | 5 262.8 |
| Sodium fluosilicate | 771.3 |
| Water glass | 4 673.0 |
| Furfuryl alcohol | 176.9 |
| Total | 34 026.2 |

*Mix directions*

1. Mix sands, aggregate andesite, and sodium fluosilicate for 3 minutes.
2. Mix in waterglass
3. Mix in furfuryl alcohol
4. Cure in molds at room temperature 1 day
5. Heat cure in molds at 90 °C for 10 hours
6. Before stripping, cool in molds 24 hours

[1] FA is furfural acetone
[2] BSA is benzenesulfonic acid
[3] FAED is furfural acetone-epoxy mixture
[4] PEPA is polyethylene polyamine

Table 2. —*Polymer concrete property tests (U.S.S.R.)*

**Compressive tests (see note)**

| Material | Specimen, No. | Modulus of elasticity, *E* GPa | Poisson's ratio, *r* | Compréssive strength, MPa |
|---|---|---|---|---|
| FA PC | FA C1 | 0.56 | 0.40 | 13.0 |
| | FA C2 | 1.50 | 0.25 | 8.5 |
| Average | | 1.03 | 0.32 | 10.8 |
| FAED PC | FAED C1 | 25.0 | 0.25 | 99.8 |
| | FAED C2 | 25.4 | 0.25 | 99.5 |
| | FAED C3 | | | 99.4 |
| Average | | 25.2 | 0.25 | 99.6 |
| Polymer silicate | $H_2O$ C1 | 14.8 | 0.28 | 23.9 |

**Flexural tests**

| Material | Specimen, No. | Modulus of rupture, MPa | Modulus of elasticity, GPa | Nominal shear stress, MPa |
|---|---|---|---|---|
| FA PC | FA F1 | 4.82 | 4.15 | 0.53 |
| | FA F2 | 4.52 | 5.28 | 0.50 |
| Average | | 4.67 | 4.72 | 0.52 |
| FAED PC | FAED F1 | 16.7 | 27.0 | 1.85 |
| | FAED F2 | 11.5 | 24.7 | 1.27 |
| Average | | 14.1 | 25.8 | 1.56 |
| Polymer silicate | $H_2O$ F1 | 4.46 | 19.1 | 0.49 |
| | $H_2O$ F2 | 3.87 | 20.2 | 0.43 |
| Average | | 4.17 | 19.6 | 0.46 |

Table 2. —*Polymer concrete property tests (U.S.S.R.)* – Continued

| Tensile splitting tests | | | Shearbond strength tests | | |
|---|---|---|---|---|---|
| Material | Specimen, No. | Tensile strength, MPa | Material | Specimen, No. | Strength, MPa |
| FA PC | FA T1 | 1.62 | FA PC | FA PC 1 | 1.12 |
| | FA T2 | 1.57 | | FA PC 2 | 1.25 |
| | FA T3 | 1.74 | Average | | 1.18 |
| Average | | 1.64 | | | |
| FAED PC | FAED T1 | 7.72 | FAED PC | FAED 1 | 5.82 |
| | FAED T2 | 8.76 | | FAED 2 | 4.20 |
| | FAED T3 | 9.10 | Average | | 5.01 |
| Average | | 8.55 | | | |
| Polymer silicate | $H_2O$ T1 | 2.28 | | | |
| | $H_2O$ T2 | 2.09 | | | |
| | $H_2O$ T3 | 2.26 | | | |
| Average | | 2.21 | | | |

Table 2. —*Polymer concrete property tests (U.S.S.R.)* – Continued

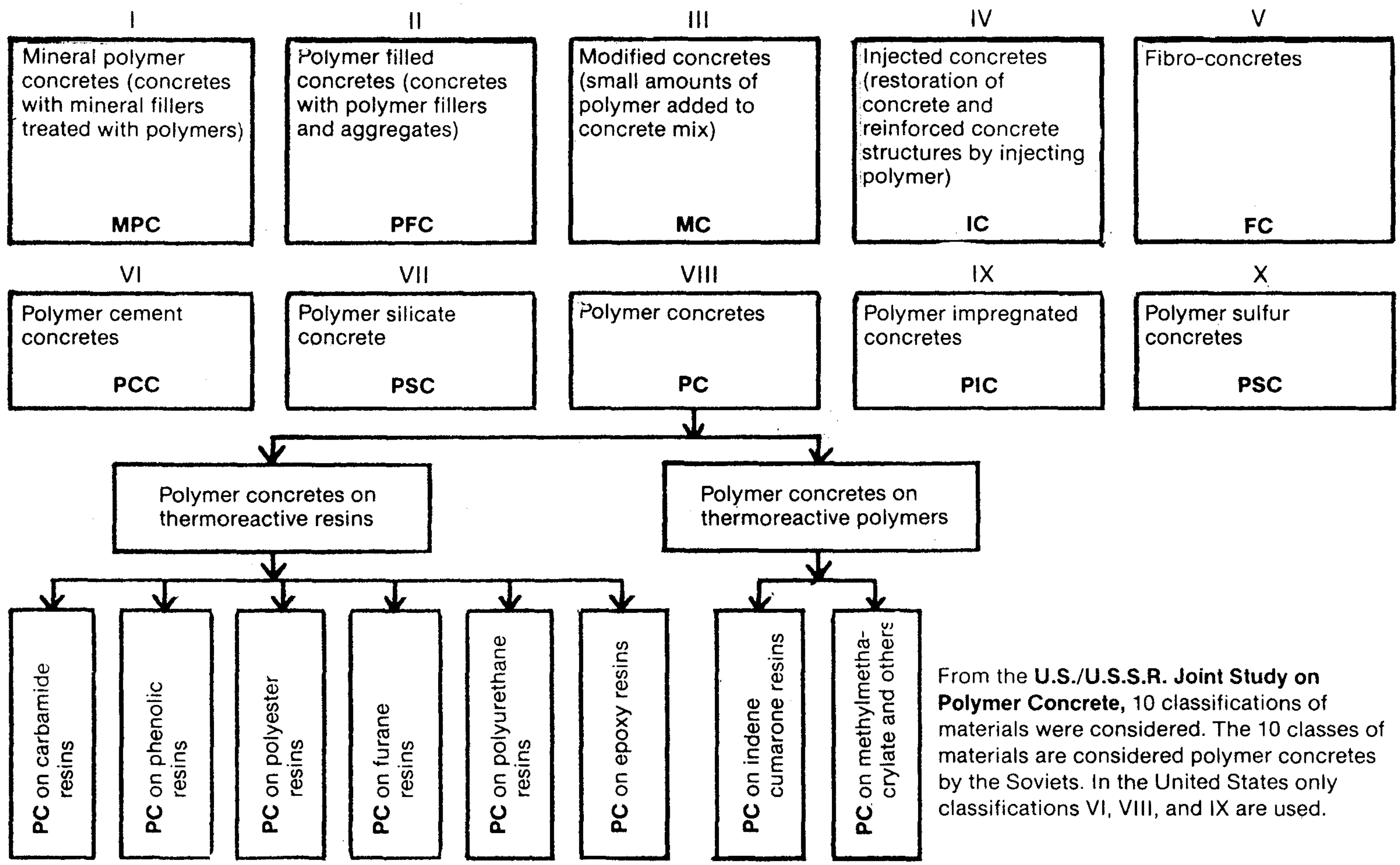
| Double shear strength | | | Other physical properties | | | |
|---|---|---|---|---|---|---|
| Material | Specimen, No. | Strength, MPa | Material | Relative mass density | Water absorption, % | Coefficient of thermal expansion, (m/m)/°C |
| FA PC | FA PC 1 | 26.4 | FA PC | 2.25 | 1.86 | $9.17 \times 10^{-6}$ |
| | FA PC 2 | 25.8 | FAED PC | 2.66 | 0.26 | $15.79 \times 10^{-6}$ |
| | FA PC 3 | 31.7 | Polymer | | | |
| Average | | 28.0 | silicate | 2.15 | 6.68 | $5.54 \times 10^{-6}$ |
| FAED PC | FAED 1 | 44.9 | | | | |
| | FAED 2 | 41.2 | | | | |
| | FAED 3 | 45.2 | | | | |
| Average | | 43.8 | | | | |
| Polymer silicate | $H_2O$ 1 | 11.5 | | | | |
| | $H_2O$ 2 | 9.2 | | | | |
| | $H_2O$ 3 | 9.8 | | | | |
| Average | | 10.2 | | | | |

Note:
FA is furfural acetone.
FA PC is furfural acetone polymer concrete.
FAED PC is furfural acetone epoxy polymer concrete.
Polymer silicate is an acid resistance polymer concrete made with waterglass, furfuryl alcohol, andesite, sodium fluosilicate, and aggregate.
C1, C2, and C3 are for compressive tests, where 1, 2, and 3 are the specimen numbers.
F is for flexural tests.
T is for tensile splitting tests.
$H_2O$ 1 is polymer silicate concrete specimen No. 1, etc.
Flexural tests were on 75- by 75- by 400-mm cylinders.
Splitting tensile tests were on 75- by 150-mm cylinders.
Compression tests were on 150- by 300-mm cylinders.
Shearbond tests were on 50-mm cores.
Water absorption, relative mass density, and double shear tests were on 50- by 100-mm cylinders.

Table 3. —*Polymer-impregnated concrete (U.S.S.R.)*

| Compressive test | | | |
|---|---|---|---|
| U.S.S.R. Specimen, No. | Strength, MPa | Modulus of elasticity, *E* GPa | Poisson's ratio, *r* |
| PIC-1 | 117 | 41.6 | 0.25 |
| PIC-2 | 133 | 42.6 | 0.21 |

Note:
Tests were done on 75- by 150-mm cylinders. Bureau concrete was impregnated with U.S.S.R. methyl methacrylate and processed by the U.S.S.R. process.




From the **U.S./U.S.S.R. Joint Study on Polymer Concrete,** 10 classifications of materials were considered. The 10 classes of materials are considered polymer concretes by the Soviets. In the United States only classifications VI, VIII, and IX are used.

**Figure 1.–Classification of polymer concretes.**


**Figure 2.–Swelling and splitting of furfural acetone epoxy polymer concrete in 5-percent sulfuric acid. Photo P801-D-80332.**

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