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IF&P FIBROSIC™ FILTERS

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DISCLAIMER

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IF&P Fibrosic™ Filters

CONTRACT INFORMATION

Contract Number	DE-FG02-92ER81349
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Contract Project Manger	Paul M. Eggerstedt
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Period of Performance	July 27, 1992 to February 17, 1995

Schedule of Milestones

Program Schedule

	1992	1993	1994	1995
Phase 1	**********			
Phase 2	***********************			
Candle Strength Testing	**************			
Tubesheet Strength Testing	***************			
Corrosion Studies	*****			

OBJECTIVES

The primary objective of this SBIR research program is to increase the performance, durability, and corrosion resistance of lightweight filter candles and filter tubesheet components (Fibrosic™), fabricated from vacuum formed chopped ceramic fiber (VFCCF), for use in advanced coal utilization applications. Phase I results[1] proved that significant gains in material strength and particle retentivity are possible by treatment of VFCCF materials with colloidal ceramic oxides. Phase II efforts will show how these treated materials tolerate high temperature and vapor-phase alkali species, on a long-term basis. With good durability and corrosion resistance, high temperature capability, and a low installed and replacement cost, these novel materials will help promote commercial acceptance of ceramic candle filter technology, as well as increase the efficiency and reliability of coal utilization processes in general.

BACKGROUND INFORMATION

Ceramic candle filtration is an attractive technology for particulate removal at high temperatures. Due to their simple and cost effective design, temperature capability, and high filtration efficiency, ceramic candles are one of the few clean-up technologies which can consistently meet gas turbine manufacturer's inlet particulate requirements and Clean Air Act mandates. Unfortunately, traditional ceramic candles, made from granular silicon carbide, etc., can be prone to failure from physical and thermal shock as well as chemical attack. These candles also tend to be expensive and, owing to their weight, present internal filter design problems.

VFCCF Filter Materials

Unlike traditional filter candles, VFCCF filter candles offer unique properties for use in HGCU applications, as shown below:

VFCCF Filter Candle Properties:

- Formed from stable ceramic oxides
- Lightweight
- High temperature capability
- Fibers & binder share similar thermochemical properties
- "Knitted" pore matrix

Typically, VFCCF filter candles are formed from commercially available fibers and binders, using existing vacuum forming technology, resulting in a low cost product with excellent manufacturing uniformity and quality control. Because the fibers and binders are essentially a blend of stable, pure ceramic oxides, such as alumina and aluminosilicate materials, the amount of contaminants, organics, etc. which might be reactive in certain applications is negligible.

With apparent density values in the range of 17-22 lbs/ft^3, VFCCF candles are much lighter in weight than their granular ceramic counterparts. This low density, which translates into a weight savings of 70-80% over isostatically pressed silicon carbide filter elements, results in a highly permeable filter with roughly twice the pore volume as granular filter candles. Additionally, as a direct result of the weight savings, the design and construction of the tubesheet and supporting hardware becomes a much easier task, not to mention the reduced stress on the filter candle flange.

VFCCF fibers and binders are typically rated for a maximum temperature of 2600°F to 2800°F, and do not exhibit significant physical changes, such as shrinkage, until a temperature of about 2300°F. is reached. As a result, they are suitable for use in nearly all IGCC and PFBC applications, where temperatures are generally 2000°F. or lower.

Because VFCCF binders are nearly identical in chemical composition to that of the fibers, differences in thermochemical properties between the binder and fiber are negligible, resulting in excellent thermal shock and thermal spalling resistance, as well as resistance to microcracking caused by differences in the thermal expansion coefficients of the fiber and binder. As a consequence of the fiber geometry within the VFCCF matrix, these candles also have an inherently high crack resistance, due to the "knitting" tendency of the fibers during fabrication, and their random orientation which tends to blunt microcrack propagation. Table 1 summarizes these important properties of VFCCF materials.

In the course of fabrication of VFCCF candles, it was found that such materials respond extremely well to treatment with colloidal ceramic oxide materials, which can increase strength, add corrosion resistance to suit a given application, and allow for the particle retention of the filter element to be controlled, all of which have led to the research effort discussed in this report. With their combined high temperature capability, low thermal expansion, corrosion resistance, and resistance to catastrophic failure, VFCCF materials show promise for use as filter candles and other internal filter hardware, such as a tubesheet, with proper colloidal treatment.

Table 1. VFCCF Material Properties

Typical Chemistry	35-60% Al_2O_3 40-65% SiO_2
Apparent Density	17-22 lbs/ft^3
Maximum Use Temperature	2800°F
Thermal Conductivity (1500°F)	1.26 BTU-in/ft^2-°F-hr
Permanent Lineal Shrinkage (2000°F)	less than 0.8%
Coefficient of Thermal Expansion	2.8 x 10^{-6} in/in-°F

PROJECT DESCRIPTION

Phase 1 Efforts

The overall objective of the Phase 1 effort was to determine which colloidal ceramic oxides of those tested exhibited the greatest increase in the strength of VFCCF filter candle and tubesheet specimens. In the case of VFCCF filter candles, strength increases were valued as important, but not at the expense of acceptable permeability. A total of five different colloidal ceramic oxides, applied using two distinctly different methods, were investigated as shown in Table 2.

Table 2. Colloidal Ceramic Oxide Tests

Materials Tested	Application Methods
Silica Alumina Zirconia Yttria Ceria	Spray Infusion

The materials above were selected on the basis of their temperature capability, corrosion resistance, thermal expansion compatability with VFCCF materials, commercial availability, and cost. Application methods were approached from the standpoints of reproducibility of results, relative cost, and minimal complexity. In both application methods, variations in the colloidal material concentrations as well as the total amount of material applied to the candle and tubesheet test specimens were evaluated in an effort to optimize a technique for producing filtration components with superior performance characteristics.

Phase 2 Efforts

Several goals of the Phase 2 effort are expected to be met as a result of this ongoing research, namely:

- Selection of the most suitable colloidal ceramic oxide material for use in increasing VFCCF material strength and corrosion resistance, without greatly sacrificing permeability (in the case of filter candle applications);
- Development and optimization of the most promising colloidal ceramic oxide

application methods, suitable for mass production of VFCCF components;

- Development and refinement of other means of increasing strength and durability of VFCCF materials, including such techniques as:

  -Filter candle flange, end-cap, and forming die modifications;
  -Investigating the effect of varying fiber type and fiber length on VFCCF material strength;
  -Investigation of lamination and joining techniques for structural VFCCF uses.

Descriptions of each of the above aspects of this research effort follow.

Colloidal Ceramic Oxide Material Selection. In addition to the colloidal oxide materials cited earlier, Phase 2 tests involving colloidal mullite were performed, and appear to be particularly promising. Colloidal mullite has good thermochemical properties and corrosion resistance, adds considerable strength, and tends to form a desirable divergent, acicular pore structure within the VFCCF candle matrix after infusion and subsequent curing. Several VFCCF filter candle specimens prepared in this manner were tested in a PFBC application at Argonne National Laboratory, through funding from the Illinois Clean Coal Institute (ICCI), with excellent results[2], other similarly prepared candles are being tested for permeability decay and durability at Acurex Corp. in Mountain View, CA.

Colloidal Ceramic Oxide Treatment of VFCCF Materials; Spray Application Trials. In continuation of the Phase 1 effort, colloidal ceramic oxides have been applied to aluminosilicate VFCCF matrices, both singularly and in combination, by spraying and immersion application techniques in the Phase 2 effort. In the case of application of colloidal oxides by spraying directly onto VFCCF specimens, a number of problems were encountered, including clogging of the spray nozzles due to drying of the ceramic oxide solids within the nozzle during application. Another problem noted during spraying was a gradual but evident dimensional change of the spray nozzle, presumably due to erosion caused by the ceramic oxide's high velocity through the nozzle orifice. This resulted in an increase in deposited material on subsequent samples, over time.

A third problem noted with the spraying technique was that it provided only a very superficial coating of ceramic oxide material onto the sample. This was alleviated partially by the use of a slight amount of vacuum on the downstream side of the specimen, but the additional amount of ceramic oxide coating observed on each specimen was very small. Efforts were made to produce very fine spray patterns for greater penetration of the colloidal oxides into the VFCCF matrices, but this was found to be troublesome and produced substantial amounts of "overspray" due to the fineness of the spray droplets.

Immersion (Infusion) Application Trials. By comparison, application of the colloidal ceramic oxides by means of simple immersion (infusion) was much more successful and easier to control. Limited to only a few variables, namely the concentration of the ceramic oxide material and the infusion duration, the application from one specimen to the next was found to be much more uniform and predictable than application by spraying techniques.

VFCCF Filter Candle Development Program. In addition to the work involving colloidal ceramic oxides, other means of increasing the durability of VFCCF filter candles has been ongoing, as part of this research grant. Geometry changes in the critical flange and end cap zones has been one successful approach. A female vacuum forming die was constructed to permit forming of an integral candle flange, in order to eliminate the original bonded flange design, which subjected the flange joint to shear when positioned in a tubesheet. In so doing, it was believed that the filter element would be inherently stronger in the flange area, by the complete elimination of the ceramic adhesive joint. Several dozen filter candles were made using the new forming die, but it was found that in every case, the tapered flange section of the filter candles did not form sufficiently thick to permit machining to the traditional (rectangular or hemispherical) flange shapes which are accepted commercially. In spite of repeated attempts using different vacuum forming pressures, flowrates, and slurry concentrations, a wall thickness of only 7-10mm resulted in the tapered (flange) section of the die.

In view of the above, the approach whereby the outside flange taper would simply be machined to the desired flange geometry was modified. Numerous designs and procedures were tested, but the most promising approach involved the following flange assembly steps:

- Truncating of the "as formed" filter candle at a point 25mm from the onset of the flange taper;
- Machining of a flange "ring" from VFCCF board stock. The outside surfaces of the flange ring can be easily machined into a hemispherical, reverse hemispherical, or rectangular flange geometry from the flat (board) stock, while the inner surface of the ring is machined to the same pitch as the outer taper of the filter candle flange. In so doing, it was found that machining from VFCCF flat stock, subjected to an immersion (infusion) treatment of colloidal ceramic oxide material resulted in a smoother outer machined surface, as compared to flanges machined from untreated VFCCF flat stock;
- "Roughing" the filter candle tapered surface as well as the flange ring inner surface to provide the best "bite" for the ceramic adhesive, followed by vacuuming of fiber debris;
- Affixing the flange ring to the tapered section of the filter candle by slipping it across the distal candle end and into place at the candle taper. A properly selected aluminosilicate ceramic adhesive, designed specifically for VFCCF materials is applied to both mating surfaces, which are first prewetted with colloidal silica for maximum adhesive penetration.
- Compression is applied to the flange joint during the curing step, at temperature, per the adhesive manufacturer's recommendations.

By following the above procedure, a substantially stronger filter flange results, since the flange adhesion joint is no longer subjected solely to shear and tension but is instead in compression, due to the flange taper. Also, unlike the "integral" flange concept, turning of the filter candle flanges to their desired final geometry (on a lathe) is not required.

In destructive testing of the compressive flange joint described above, a downward (shear) load of 73 lbs. was applied to the filter candle flange before failure occurred. Additionally, as hoped, the failure did not occur at the glue joint seam but instead failed within the porous section of the candle. This compares quite favorably to earlier flange designs tested in Phase 1, which had an average flange strength of 53 lbs. Further efforts are underway to increase the flange strength to an even greater degree; ceramic adhesives using reconstituted fiber, for example, appear to show promise in creating a unique "ceramic weld" between the joined surfaces.

With the above advances made in the flange area of the filter candle, it became apparent that similar candle fabrication techniques would be applicable to the end cap section of VFCCF candles. Capitalizing on the techniques used above, a compressive-state glue joint in the end cap area was developed. By rewetting the open filter candle end temporarily, it became possible to insert a conical VFCCF plug into the softened end to serve as an end cap, much like a stopper in a flask. By inserting the plug backwards (i.e., widest end first), however, the softened cylinder could then be drawn or "puckered" around the conical taper of the plug, after which it would reharden upon drying. Further use of some of the techniques used during flange assembly resulted in a design which places the end cap joint in compression, rather than shear, during the critical jet pulse cleaning of the filter candle.

RESULTS

Phase 1 Efforts

Phase 1 test results showed that the bending and compressive strength characteristics of VFCCF materials can increase substantially as a direct result of the infusion of colloidal ceramic oxide suspensions into the VFCCF matrix. In some instances, it was possible to increase strength of typical VFCCF tubesheet specimens eight-fold, in comparison to the strength of untreated specimens. By variation in colloidal solution application techniques and curing methods, it was also possible to greatly increase VFCCF filter candle strength in critical flange and end cap areas, with a minimal decrease in overall candle permeability. Table 3 provides the highlights of some of the infusion trials, which were quite successful.

Table 3. Results of Phase 1 Testing
Aluminosilicate VFCCF Tubesheet Specimen Strength Test Results After Colloidal Ceramic Oxide Infusions

Infusion Description	Apparent Density (lbs./ft.^{3})	Modulus of Rupture (lbs./in^2)
Untreated Aluminosilicate	17.02	52.68
Single Immersion, SiO_2	36.83	274.11
Single Immersion, Al_2O_3	32.67	127.84
Double Immersion, SiO_2, then Al_2O_3	47.06	440.45
Single Immersion, ZrO_2	32.08	61.79
Single Immersion, Y_2O_3	28.81	168.15
Single Immersion, CeO_2	30.84	86.1

Phase 2 Efforts

Single Infusion Studies. Because of the problems cited earlier with the application of colloidal ceramic oxides by means of spraying, Phase 2 efforts focused primarily on infusion (immersion) as the method of application. Numerous single infusions of VFCCF (aluminosilicate) fiber specimens were made; in each case, the solids concentration of the various colloidal suspensions used was as follows:

- Silica 40% w/w
- Mullite 28% w/w
- Yttria 14% w/w
- Alumina 20% w/w

While it would have been desirable to test using identical concentrations of each suspension, the number and significance of other variables (e.g., pH, viscosity, particle size distribution, etc.), combined with the relative instability of the suspensions, made this an impossible task. Also, unlike Phase 1 testing, ceria and zirconia colloidal ceramic oxides were eliminated in the Phase 2 tests, due to their relatively small resultant strength enhancement of VFCCF matrices.

In the case of silica, a single immersion appeared to increase weight and also strength of the aluminosilicate fiber matrix considerably more than any other material, but at the same time appeared to "seal" the outer pores of each specimen so as to prevent further penetration of colloidal oxides after a subsequent immersion. Although silica is known to increase VFCCF material strength dramatically, because of its susceptibility to corrosion in high temperature environments (from steam, alkali and other corrosive attack mechanisms), it became apparent that another additional ceramic oxide must be applied over the silica layer to produce a durable product. Because of the sealing tendency of the silica, however, it became questionable if suitable penetration by a subsequent corrosion resistant material such as alumina, yttria, or mullite would in fact take place.

Another material which was tested in a single treatment immersion application was that of colloidal mullite. While the mullite applications did not see the rather dramatic weight or strength increases observed with the silica treatment, it was noted that the mullite treatment penetrated very uniformly in each specimen tested, and did not have the tendency to seal or "blind" the pores, as was noted in the silica immersion trials. This observation seems to indicate that subsequent immersions in colloidal mullite, or other colloidal ceramic oxides might lead to greater overall penetration than was noted in the silica trials. Given the advantage mullite has over silica in terms of corrosion resistance, (particularly against vapor phase alkali species in a hot gas environment), combined with good thermal shock resistance and low thermal expansion, mullite is considered to be a choice colloidal material for VFCCF treatment. In each test case involving mullite, a weight increase of 45-85% was noted.

Still another material which was tested in a single treatment immersion study was that of alumina. Alumina has a very high corrosion resistance with regard to vapor phase alkali species, but it was noted that the amount of alumina infused into the VFCCF specimens resulted in a weight increase less than that of mullite, in the range of 45-65%. Based on Phase 1 bending strength test data, alumina did not significantly increase strength, so it was concluded that the use of colloidal alumina for VFCCF materials would be limited to that of a final corrosion resistant treatment only.

The last colloidal ceramic oxide material which was applied by means of single immersion techniques in the Phase 2 effort was that of yttria. Yttria has high thermal stability and good corrosion resistance, but exhibited relatively small weight increases, generally averaging about 40%.

In summary then, the strength of structural VFCCF aluminosilicate materials can be substantially increased by a single immersion in silica, whereas strength and corrosion resistance may be increased in one (or more) immersions using mullite colloidal ceramic oxide material, possibly in conjunction with colloidal yttria or alumina.

For filter candle applications, in contrast to structural ceramic applications, it appears as though the mullite colloidal material also provides a strength increase without a dramatic reduction in pore size,which relates inversely to the pressure differential across a filter candle in operation. Specifically, in the case of the single mullite immersed filter candle specimens, it was found that a weight increase occurred on the order of 60-80%, for immersion durations of 10-15 seconds. Unlike silica, however, it was found that the pore structure of the material did not change dramatically and decreased only from approximately 55 microns to 45-50 microns, from which it can be concluded that filter candle specimens could undergo dramatic increases in strength and durability, as well as corrosion resistance, using a colloidal mullite material, without greatly compromising the pore size (and consequently the pressure differential) across the filter candle. Ongoing tests seem to show that even diluted concentrations (as low as 12%) of mullite are very effective in enhancing candle strength, with almost no loss in permeability.

VFCCF Fiber Length Variation; Mullite and High Alumina Fiber Testing. Efforts involving variations in VFCCF fiber length, as well as forming of filter components using mullite fiber and alumina fiber, rather than aluminosilicate fiber, were performed to see what effect these changes might have on VFCCF material strength. The comparative testing was limited to three-point modulus of rupture (M.O.R.) bend tests, performed on specimens having dimensions of 3" x 2" x 12" (span). The average strength values from these tests are shown in Tables 4 and 5.

Table 4. VFCCF Fiber Length vs. Strength

Nominal Fiber Length (mm)	Modulus of Rupture (psi)
30	55.35
15*	55.65
7.50	85.95

*This material is our VFCCF "standard" material.

Table 5. VFCCF Fiber Type vs. Strength

Fiber Type (Nominal Length, mm)	Modulus of Rupture (psi)
Aluminosilicate, 15mm	55.65
Mullite, 15mm	24.30
High Alumina, 15mm	48.15

The above results indicate that longer aluminosilicate fiber lengths, which produce a lower density product, do not increase strength in comparison to the standard (medium length) aluminosilicate fiber normally used. Shorter, high density aluminosilicate fibers, however, appear to increase strength substantially, by approximately 55%. In the case of the various fiber types tested, both the pure mullite fibers and high alumina fibers show lower strength values than the standard medium length aluminosilicate fiber.

Ceramic Fiber Composite Materials (for structural applications). Investigation of a commercially available pressure-laminated aluminosilicate fiber composite material has also been underway as a result of this research effort, for use as a suitable material for hot gas filter structural components. The composite material closely matches the chemical composition of VFCCF aluminosilicate boards, but has improved properties both in compression (10,000 psi strength) and tension (8,000 psi strength).

Thicknesses are commercially available up to a maximum of 1", and sizes of up to 36" square can be obtained. Because of the size limitations, however, the joining of sections of this material is required to fabricate ceramic tubesheets, etc. in excess of about 36" in diameter. For filter applications involving large tubesheet designs, a joined tubesheet eliminates several drawbacks associated with monolithically formed tubesheets, namely:

- The tendency for formation of air pockets, poor fiber "knitting", etc. in VFCCF specimens thicker than about 2";
- Inability to vacuum form, dry, and cure large diameter specimens, due to existing equipment size limitations (tanks, dies, ovens, etc.);
- Inability to physically handle large specimens while wet, due to their fragility.

In view of the above, the concept of laminating and joining composite ceramic fiber board sections to create a larger final product is being pursued; the 18" x 30" laminated tubesheet specimen shown in Figure 1 is currently being tested for high temperature creep strength at Acurex Corp. of Mountain View, CA.

In addition to high strength, advantages of laminated and joined composite ceramic tubeheets include:

- Utilization of "off-the-shelf" VFCCF and composite board materials for maximum product uniformity, tolerances, etc.;
- No special oversize dies, ovens, tankage, etc. required;
- Attractive cost;
- No special one-of-a-kind tooling required for each particular product design;
- Chemical stability, corrosion resistance, and thermal expansion properties similar to VFCCF materials;
- The need to stock only laminated boards and ceramic adhesive for virtually any tubesheet application.

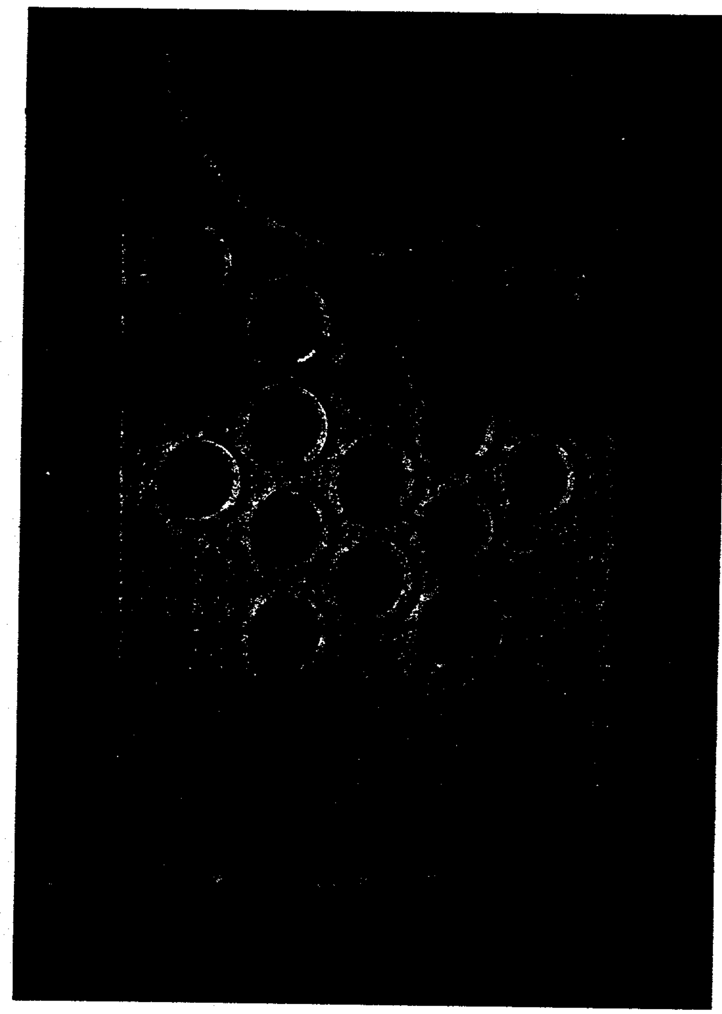

Figure 1. Laminated Composite Ceramic Tubesheet Section

Conclusions

As evidenced from the preceding sections, mullite appears to be the most promising colloidal ceramic oxide treatment material for VFCCF matrices. When applied by means of infusion techniques, considerable process control can be maintained with relative ease, for consistency of final product. Colloidal mullite can be used to increase the strength of VFCCF filter candles without a significant decrease in candle permeability, and creates a desirable divergent, acicular pore geometry during high temperature curing.

The development of a new flange and end cap design approach and joining technique appears to be very promising; continued efforts in ceramic adhesives development should lead to even greater filter candle integrity.

Aluminosilicate fiber composite materials, for use as lightweight ceramic structural components, offer high strength and can be successfully laminated for even greater strength, using proper joining techniques and ceramic adhesives suited for VFCCF materials.

FUTURE WORK

Future VFCCF filter candle developmental efforts will consist of:

- Investigation of multiple infusions of colloidal mullite material, as well as successive mullite/alumina and mullite/yttria infusions, to maximize filter candle strength and corrosion resistance without the premature sealing of pores and possible corrosion, as was noted with colloidal silica;
- Continued development of critical filter flange and end cap areas;
- Further investigation of shorter (7.5 mm) length aluminosilicate VFCCF fibers for use in increasing filter candle strength;
- Application of a finely chopped ceramic fiber "membrane" layer on the filter candle, to produce superior filtration characteristics;
- Corrosion and alkali exposure studies of the most promising filter candle specimens as a result of the above.

Regarding VFCCF and aluminosilicate composite materials, for structural (tubesheet) applications, future efforts will include:

- Development of the optimum lamination, joining, and curing procedures for maximum strength and integrity of these critical components.

REFERENCES

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