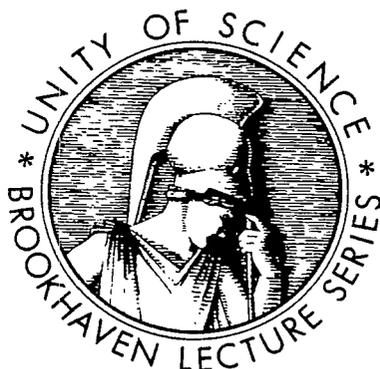


Transcript of:
339th Brookhaven Lecture
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“Rendering Asbestos Harmless”

Dr. Leonidas Petrakis
Department of Applied Science



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"We are here for this -- to make mistakes and to correct ourselves, to stand the blows and hand them out. We must never feel disarmed: nature is immense and complex, but it is not impermeable to the intelligence; we must circle around it, pierce and probe it, look for the opening or make it."

Primo Levi, *The Periodic Table*

Introduction of the Speaker

James Davenport, Chair, Department of Applied Science: "It is always a pleasure to introduce someone from the Department of Applied Science and I guess the more so since Leon proceeded me in this job. He received his Ph.D. in Chemistry from U.S.C. Berkeley. He has taught at a number of places including the Univ. Of Maryland, but he spent about 25 years actually doing industrial research at two different places; at Chevron and at Gulf. He of course is known to us first because he came here approximately ten years ago to chair our department, as I mentioned. He did not come though completely unknown, he has by now been the author or the editor of some six books and over 130 papers actually in his field of expertise, which includes work on catalysis for example and some early work on NMR. I also want to mention that he coauthored with Rita Colwell, which has just been named the Director of the National Science Foundation, and who served on our DAS visiting committee a number of years ago and provided some helpful advise and input to us. Part of that collaboration was a book called "Petroleum in the Marine Environment", which they coauthored. He has indicated to me too that although I have not seen this actually, that he wrote a brief monograph on *Pollution in the Athens Basin*, and I'm not sure... 'Is that in Greek, or is that in...?'... so, I probably wouldn't be able to read it directly anyway. And, in 1997 he published a historical novel about growing up in Nazi occupied Europe. Actually, he has an interest in poetry and a few weeks ago, he promised to send me a poem, which he hasn't sent yet, so I hope I'll be receiving that soon... not yet... hold on one minute. What I really want to say though is that all of us actually, most of us for sure who've been here over the last couple of years recognize that for the last year or so at a time when a lot of the news that made the newspapers at this Laboratory was bad news, we had a few things and of course the work with PET comes to mind, but in addition the work on asbestos which is what Leon is going to talk about comes to mind, as examples of good news that came out of this Laboratory, things that we did which were helpful. He was recognized for this by many people. It was recognized within the DOE and was also recognized as high as the Secretary level. So.. Leon... Thank you."

Rendering Asbestos Harmless

339th Brookhaven Lecture

November 2, 1998

Leon Petrakis: Thank you, Jim. I appreciate the invitation from the BNL Lecture Committee to share with the BNL community what we have done in the asbestos project, which I was privileged to lead during the last four years. Last December, as Jim indicated an interesting month in a very "interesting" year for the Laboratory, there was a joint public announcement between the Laboratory and W.R. Grace & Co. regarding a new process that the two institutions developed to deal with asbestos. That announcement was the culmination of a 15 million dollar, four-year effort, jointly funded by W.R. Grace & Co (to the tune of over 12 million dollars) and the U.S. Department of Energy which put up approximately another 3 million dollars. The announcement came at a difficult time and, given the controversial nature of asbestos, it was not surprising that it received a great deal of attention, both in the U.S. and also outside, both by scientific media and media in general. I was interviewed by the *New York Times*, the *Wall Street Journal*, *Le Monde* in Paris and so on. Closer at home, both Channel 12 and *Newsday* took notice of the announcement that the Laboratory made. In fact, *Newsday* wrote an editorial, which I would like to put-up for a second (**Figure 1**) : "**Brookhaven Breakthrough; By Solving the Asbestos Disposal Problem, the National Lab Proves again its Value**" --and I have underlined one of the sentences: "*The Breakthrough could not have come at a better time for embattled federal facility. It adds new luster to the reputation of the Laboratory, which despite recent attempts to transform it into a political football --is an regional treasure.*" Perhaps it is a bit self-serving putting it up, but I think it reflects on the Laboratory, so I have no qualms about doing that. I would also like to show a bit of the piece that Channel 12 showed, for two reasons, one it sets the background for what I want to do for the next 45-50 minutes, but also it is a very brief summary of the technology that came from that effort. So, I will show this **video (2)** here.

Channel 12 Report: "*'A breakthrough scientific discovery'-- that's what scientists at Brookhaven National Laboratory are calling --a revolutionary asbestos cleanup method as News 12 Nicole Bell reports that's been said the new procedure is cheaper and quicker than what has been done before. Nicole Bell speaking: It's being hailed as the first product in the world capable of safely destroying asbestos in installed fireproofing. It's a shaving-cream type substance that when applied digests asbestos fibers and dissolves them into harmless minerals. After three and a half years of research that has been developed by scientists at Brookhaven National Laboratory'. (Continue....) Leon Petrakis now speaking on Channel 12: 'The application of chemicals is very gentle, compared to the scraping and therefore, there are almost no fibers released. And the fibers being released are fewer..10 to 100 times lower than of the current practice. '... Nicole (Channel 12 reporter): 'Of course asbestos was commonly used in fireproofing in structures built in the 1950's and 60's. It has more recently been blamed to rare forms of lung cancer. This new technique is said to be safer, slash the time it takes to remove asbestos by days and costs just a*

fifth of the price of the old method of scraping the material out of fireproofing."

Actually one other aspect that comes from showing that video, is that one has to be very careful about what you get from television, as we all appreciate --they did not quite get my name correctly... some of you may have noticed...

Asbestos. We will do a very quick lesson in Greek, if I may (Figure 3). *Asbestos* is a Greek word, *Asvestos*, coming from the *negating alpha* and the classical Greek verb *svenynai*, to extinguish. So, *asbestos* literally means *inextinguishable*. Of course, *asbestos* has terrific thermal insulation properties and fire retarding properties, so the name *inextinguishable* is a euphemistic name in the same sense that Magellan called the Pacific Ocean '*Pacific*', which was nothing like that when he first entered. The word *asbestos* first appears in a classical text by Theophrastos in the fourth century B.C. Theophrastos was one of the students of Aristotle.

In the last few years, the word '*Asbestos*' has achieved a great deal of notoriety. Periodically we see articles in the *New York Times*, here is one for example (Figure 4) A 1995 article, '*Brooklyn School Races to Clean-Out Asbestos*', another one from the *Times* again (Figure 4a), and, this I think is a quintessential New York picture... There was a problem on the Upper East Side and space-suited workers are trying to deal with the problem outside this restaurant, while this cool New Yorker inside seems to be enjoying her meal and her crossword puzzle. Of course, this is not a U.S. phenomenon alone. Negative reaction to the word *asbestos* seems to be universal among many folks. In 1995, I spent a brief sabbatical at the University of Paris and *Le Monde*, another distinguished newspaper, had this interesting article (Figure 5) discussing the *asbestos* situation in the UK and France and attempting here to establish a correlation between the imported *asbestos* in France and the number of deaths from mesothelioma. Actually, at the time I was in France in 1995, there was a great deal of friction between, on one hand, the administration of the University of Paris and on the other between the students and unions.

Of course this notoriety of *asbestos* is rather a recent development. *Asbestos* had a great deal of fame before that. It had entered the commercial sector quite extensively. The U.S. Environmental Protection Agency reported that in the 70's there were over 3,000 commercial products that were based on *asbestos* (Figure 6). By far, the most extensive was in insulation fireproofing of buildings as well as thermal insulation of pipes and also in other building materials. There were other kinds of interesting articles, woven articles from cloaks to theater curtains to even shrouds; of course the automobiles have used *asbestos* quite extensively in brake and clutch linings. During the Second World War, *asbestos* was classified as strategic materials, so it was stockpiled because there was difficulty to access with only three countries producing the material --Canada, South Africa and Russia. And, there had been interesting miscellaneous items, battens, telephones, there were filters, and this is a very interesting one, a cigarette filter, and apparently it turns out there is a synergy in lung disease when tobacco smoking is combined with the *asbestos* filter. I guess this was established after the fact. So, it was very extensively used until the 70's when the U.S. Environmental Protection Agency classified *asbestos* as a regulated material. OSHA followed-suit and established their own rules for the protection of workers in the work place. This regulations came about as a result of concerns with the health implications of

the use of asbestos (**Figure 7**). It turns out that the health implications had been commented upon quite early. Pliny the Younger in the second century AD had noticed the increased occurrence of disease in asbestos workers. In the late 19th century high death rates were noted among French and English asbestos workers dealing with weaving and courting. By 1927, asbestosis had been identified, which is known to produce scarring of lung tissue. Then in the 30's bronchial carcinoma was identified and then by 1960 mesothelioma, which is a form of cancer generally not seen in the general public, but almost exclusively in asbestos workers. It is a cancer of the lining of the thoracic or the abdominal cavities. Amphiboles, one of the two common forms of asbestos, and I'll discuss that in a second, have been implicated, although there is some controversy as to the exact form of asbestos that is responsible for the lung disease. The U.S. Regulatory agencies bypass that and the rules apply uniformly to all asbestos fibers. The peak production a couple of decades back was almost 5 million metric tons, most of which is **chrysotile**, one of the two very common forms of asbestos. The other is **amosite** and it will come to those structures and the their activities in a moment.

Atmospheric concentrations have been found to be 10-100 nanograms per cubic meter of air, near factories there had been much higher concentrations. Two numbers I will ask you to retain for the duration of this talk: one is the '*permissible emission limit*' (*PEL*) that EPA and OSHA have put at 0.1 fiber per cubic centimeter of air, while materials which have less than 1% asbestos are considered non-asbestos containing material. Anything above 1% is *asbestos containing material*. (**Figure 7A**). So if you are going to deal with asbestos according to the Regulatory Agencies, you have to take it to that level of the 1% or below.

Asbestos is really a generic name for a series of minerals and like all minerals it has a wide range of compositions and structures (**Figures 8, 9**). The two common forms are **amphiboles** and the other is **serpentine**s. Both of them are silicates. The amphiboles are double chains of silicates with a considerable amount of iron and some magnesium (**Figure 10**). The common form of amphiboles, amosite, is about 10% of all the asbestos that has been mined. And amosite has gone traditionally in thermal insulation, piping, so both DOE and the utility companies have a very significant problem with amosite. And in fact, DOE has an interesting problem because quite a bit of the amosite is contaminated with radionuclides, so that it is a good candidate for two technologies from Brookhaven, one is the asbestos that I am discussing and the other is the sequestration of heavy metals that A.J. Francis has developed. In **Figure 8** I am showing the refractive indexes for they have been used quite effectively to tell apart quite readily the different forms of asbestos. The second form of asbestos is the **serpentine**s, which are the layered silicate structure. Chrysotile or white asbestos is the most common form, some 90% of all asbestos that has been mined and used. Here (**Figure 9**) is a rough indication of the difference in the chemical composition of the two. Chrysotile is silicate and magnesium oxide, while amosite is silicate with a great deal of ferric oxide in there. Here is a cartoon (**Figure 10**) of the two structures, both of them the silicate, here's the amphibole with the dual silicate chain, while the serpentine are the layer structures. On the bottom part of the cartoon, there is an attempt to show the alteration of the silicate layer and the magnesium oxide layer. Actually, you have a silicon oxide layer and then a magnesium oxide, while silicon and magnesium share covalently the same oxygen, but because of the difference in the atomic radii of the two, the composition imposes a specific structure; it imposes a curvature which results in a tubular structure, which alternates the silica-magnesia,

silica-magnesia and with the top layer being the magnesium oxide, which is hydrated. Here is another cartoon (**Figures 10A, 10B**) of the chrysotile structure and this is a blown-up version again with the silica-magnesia layers, which gives a periodicity to the structure which we can exploit, and we have exploited for analytical purposes as well as product identification. But I will come into that a bit later in my talk.

In addition to the thermal and fire retarding properties of asbestos, a very distinct and important property of asbestos has been its presumed chemical inertness. It turns out that asbestos is not really that inert. It has been known for a number of years that strong acids can attack and do attack the asbestos structure. One important finding in the project that we undertook jointly with W.R. Grace & Co. was the finding that **the combination of a strong acidic function in the presence of a small amount of fluoride iron**, which acts catalytically, can be much more effective in attacking, in digesting, in destroying the asbestos structure than even the strongest acids. The exact composition of the DMA (Digestion Mixture or Material for Asbestos) that is being commercialized is based on phosphoric acid plus a boron or silicon fluoride salt as the source of the fluoride. I will come to that in a second, but for the time, I would like to discuss further the reactivity of asbestos using some chemistry that was developed at Brookhaven. If one requires that you have the acidic function plus the fluoride ion, why not use the two in the same molecular vehicle, if you will, to provide those two as a way of avoiding, for example, the generation of HF, hydrofluoric acid, which a no-no from the regulatory agencies. So early on, we proposed to W.R. Grace that we consider the superacids, but they had no interest in that. DOE/ER, one of the two sources of funding for us, allowed us to do a couple of things that were very important in the overall project. One was to develop an analytical process using the Light Source, which I will discuss presently, as well as, develop some new chemistry based on superacids.

The DMA or the phosphoric acid in the commercial process attacks chrysotile which is found in fireproofing. However, DMA does not attack the amosite or the combinations of the amosite-chrysotile which as I said are very common in thermal insulations. The chemistry that we did develop using superacids, in fact, does the job. Superacids are combinations of Bronsted acids with a fluorinated Lewis acid, and their acidity is much greater than that of pure sulfuric acid (**Figure 11, 12**). If we take the Hammett function as a quantitative measure of the acidity, sulfuric acid is 12. Then the superacids are 7-8 orders of magnitude stronger than the sulfuric acid. Phosphoric acid in combination with borontrifluoride is one example. Antimony pentafluoride, as those of you who have been close to catalytic chemistry appreciate, has been a very important source of superacidic function. In fact, Professor George Olah in 1994 received the Nobel Prize for advancing the use of superacids in catalytic reactions. If I may share an interesting tidbit, in 1993 I had co-organized with Professor Jacques Fraissard from the University of Paris an Advanced Study Institute on the acidity and basicity of solids and we had invited Professor George Olah long before he got his Prize. He gave a wonderful presentation on the superacids. I also had had some experience with superacids manipulating the structures of zeolites, but when we got together with W.R. Grace, George Olah's comments were fresh in my mind and it was of course a straight-forward kind of thing to propose that we do use the superacids in this project. Since W.R. Grace was not interested in superacids when we came back from our first visit at the W.R. Grace laboratories, I asked Toshi Sugama in DAS to do some preliminary

experiments for evaluating the potential of the superacids. The Directorate were kind enough to allow us to use a bit of some Laboratory Director's R&D funds that we had, both to pursue the chemistry as well as to use the Light Source for some product identification in the analytical method.

One of the patents that has been granted to Brookhaven is the use the superacids. I would like to use the fluorosulfonic acid as an example of the kind of changes that take place in the structure of asbestos, and although in the commercial process for fireproofing with chrysotile it is phosphoric acid that is being used, nevertheless the chemistry that I'll discuss here is quite applicable there also. In trying to understand the chemistry which is interesting in its own right, but also could provide guidance for the development for the commercial process. We did do quite a bit of work with fluorosulfonic acid and we used a number of the capabilities that exist here at the Laboratory to monitor and try to understand what was happening. We used infrared, XPS, SCM, the Light Source.

Let me show here some infrared spectrum (**Figure 13**). The top is the infrared spectrum of chrysotile and at the 3680-3640 wave number region, there are hydroxyl stretches which are characteristic of the magnesium hydroxyl and therefore can be taken as characteristics of the chrysotile. Here also at 1080, 1050, and 970, there are a number of bands which are associated, which are silicon-oxygen stretching bands with silicon-oxygen in different environments. For example, the 1080 is silicon-oxygen stretch in the silicon-oxygen-magnesium environment. The 1080 is the silicon-oxygen. The 1050 is the silicon-oxygen-magnesium and so on with the others. These are quite well studied and have been assigned with some considerable degree of confidence. In the next three traces, I am showing the the infra-red spectra from the chrysotile as it is being affected by fluorosulfonic acid at different concentrations. By the time we get to 15% fluorosulfonic acid you see all features associated with the chrysotile have been eliminated. The structure has been changed completely. The magnesium-hydroxide is gone, so are the silica bands. New bands appear at 1220 and 1090 for example which are characteristic of hydrated silica. So there is no doubt that we have completely destroyed the chemical structure of asbestos. It is very interesting to compare this to the 15% fluorosulfonic acid and 3% HF plus 14.7% sulfuric acid. This is the equilibrium value of hydrolyzed fluorosulfonic acid and you do see that the two spectra are identical, indicating that the fluorosulfonic acid, a single carrier of the acidity and the fluoride ion so you don't have to worry about using hydrofluoric acid to do the job quite nicely.

Let me show some additional infrared spectra. (**Figure 14**) These are spectra of the chrysotile which has been treated with hydrofluoric acid and you see 15% hydrofluoric acid destroyed most of the features associated with the chrysotile structure; while with 15% sulfuric acid treatment you still have a great deal of the structure intact. In fact if we use the hydroxyl stretching band in the magnesium hydroxide as a measure of the asbestos chrysotile structure, we can see (**Figure 15**) the relative effects of the 15% sulfuric acid that is quite ineffective; HF that is quite effective and fluorosulfuric acid which is most effective; and, of course, I keep coming back to this point, with fluorosulfuric acid as I'll show some data later on, we do not have to worry about about HF being present. This is an important point for the regulatory agencies for developing a process.

XRD was quite useful in identifying products and also reaching some conclusions as to what is happening (**Figure 16**). In the top I'm showing the x-ray diffraction pattern of chrysotile and again the same with increasing amounts of fluorosulfuric acid. You remember that the periodicity between the structures did predict an x-ray diffraction pattern which is observed quite nicely and of course when you go to the 15% all the features of the chrysotile are gone. Very interestingly there is evidence of magnesium fluoride that is precipitated, magnesium sulfate which is another product; and what is even more significant is the lack of any evidence that crystalline silica is being formed. Crystalline silica would be a no-no and would derail the process from going forward.

But apparently what is going on with the chrysotile when treated with fluorosulfonic acid, is shown in **Figure 17**. The fluorosulfonic acid hydrolyzes to form HF and sulfuric acid. The first layer, the outmost layer of the magnesium hydroxide is being attacked to precipitate magnesium sulfate; also there is some magnesium oxide as the additional magnesium ions are precipitated with the fluoride to form the crystalline magnesium fluoride. There is also silicon tetrafluoride which readily hydrolyzes to give more silica gel and regenerates the HF that can be recycled and act as a catalyst.

Because the regulatory agencies are concerned not only with the chemistry, but also the morphology, and as I said they do not differentiate among the different forms of asbestos, we had to look carefully at the fibers in addition to the chemical composition. Bob Sabatini in the Materials Division, DAS, obtained this very nice SEM pictures (**Figure 18**) which show clearly the fiber structure before the chemical attack, and you see they are completely gone. Also, the energy dispersive spectroscopy, at least in the top 1.5 micrometer layers, shows the type of chemicals that are associated with the structure. Clearly the chemical compositions of the fibers have been changed radically.

One problem that we faced early on in dealing with this development was how do we convince the regulatory agencies that we have destroyed asbestos? EPA specifies that the method of choice is polarized light microscopy. But, the EPA folks who developed polarized light microscopy at the Research Triangle will tell you themselves that unless very carefully done, PLM is not terribly reliable. In fact, we sent out a lot of samples to different EPA approved laboratories and we got back an incredible range of answers. We had made mechanical mixtures of asbestos using NIST samples which we were using to calibrate the analytical method. So we had to deal with **developing a new analytical method** that quantitatively could reassure us that indeed we destroyed the asbestos and we could take those data to the regulatory agencies. This was the other piece of work that DOE/ER paid for and this is where the Light Source proved invaluable in our development of the process. Here is a picture (**Figure 19**) of the X7A-Beam Line in the Light Source. This is being run by Dave Cox, whose PRT we joined for a couple of years. Joe Hriljac and his postdoc, Cahit Eylem, did this work, and, as I said, it proved extremely valuable. A method that we developed from that phase of the project has been accepted. It was published in peer-reviewed journals and the EPA accepted it as a reference method.

X-ray diffraction patterns are shown here (**Figure 20**). B is the chrysotile with this particular (002) diffraction line that reflects the periodicity of the two alternating structures being the one

that we used for quantitative analysis in conjunction with the ratio method with alumina as the standard. XRD measurements were made in the laboratory, but we found that laboratory XRD failed at around 1% or below. And we wanted to go much lower than that. Here is (Figures 21, 22) an indication of the quality of the data that the Light Source was providing with the NIST samples 1%. You see a tremendous signal-to-noise ratio for the 1%, and still quite good at the 0.1% chrysotile level. These kind of data allowed us to develop a calibration curve so that we could use it to determine that we have gone below the 1% regulatory limit, of what the regulatory agencies consider ACM (Asbestos Containing Material).

It turns out that asbestos is a very interesting material, much more reactive and I'll make the analogy again with zeolites and indicated that asbestos can be manipulated quite readily. However, the main thrust of the project was in the development of a commercial process to deal with asbestos in commercial applications. As I mentioned earlier, a main commercial use of asbestos, following the Second World War, was in fireproofing. That developed out of the use by the Navy of a sprayed-on method to insulate naval vessels as well as boilers and pipes and so on. In the 50's a similar product came to the market that typically had 10 to 20% chrysotile and the rest was filler material, gypsum, vermiculite. When the regulatory agencies classified asbestos as a regulated material, a tremendous burden was placed on building owners to deal with the problem. If asbestos fireproofing is intact and there are no fibers in there, there's really no problem. When fibers are inhaled, that is where the concern arises. So, if you have asbestos that is not disturbed, you can leave it in place, but if you want to remove it, that can be a very costly undertaking. EPA has indicated there are 750,000 structures in this country which have asbestos that needs to be dealt with --schools, high rises, hospitals and other structures.

The most effective way of dealing with that problem is first to put a plastic cocoon in the space you want to remediate, reduce the pressure as you do in a hospital room to keep the fibers inside, then space-suited workers with the appropriate masks go in there, wet down the asbestos, scrape it and then they have to remove that scraped material to a special landfill as regulated material as a considerable cost. When we started dealing with this, Marty Blume gave me a very interesting tidbit from the local scene, how a tiny building, I don't remember which one, next to the Directorate --when it was taken down, by far the greatest cost associated with it was the removal of the asbestos. And of course, for buildings you are going to save, you need to re-fireproof once you remove the old asbestos fireproofing, so there is an added expense. The expense for dealing with asbestos in this manner varies considerably from location to location. New York City is much more expensive than Idaho. But, a figure that has been thrown around is something like \$12, \$15, \$18 per square foot. That translates to something, well I have seen figures as high as \$150 Billion for the fireproofing. The more commonly quoted numbers are about \$100 Billion and about 1500 small companies in the U.S. that are dealing with the problem. At the rate at which the problem is being attacked, it will take about 25 years or so to deal with it. Then of course, you have to re-fireproof, and this is just the chrysotile fireproofing problem. The thermal insulation is a different issue, the amosite is a different issue.

W.R. Grace asked us to work with them in perhaps coming up with an innovative process to deal with asbestos. When they called me, it was on a very busy day and when they told me they had some preliminary evidence that asbestos could be treated chemically, my reaction, since I didn't

know anything about asbestos was ..., well, I thought, there is a fire-sale on a couple of bridges in Manhattan, and I would be very happy to sell them to them.... We did form a group/team -- Calvin Lynn, Allen Goland, Larry Kukacka, Joe Hriljac, Jim Hurst-- and we asked a representative from ES&H to come with us. We went to W.R. Grace after we signed a secrecy agreement to see what they had. I became tremendously excited about the possibilities. We had been working with W.R. Grace already, eventually another CRADA came from them on corrosion, and Allison Davenport and Hugh Isaacs worked on that. But, it was very interesting to see the preliminary data that they had. We called DOE/ER and they got on board very quickly about supporting us to become involved. We called DOE/EM and Clyde Frank signed on very quickly, but some of his subordinates had to be persuaded. The BNL Directorate, they were kind enough and they allowed us to use a little bit of the LDRD money to get some of the preliminary results, and so we were on our way.

The chemistry was done both here at Brookhaven and at W.R. Grace. For the physicists and the other non-chemists in here, maybe I've shown too many chemical structures, but it's good for everybody to have some chemical equations. The DMA which has been commercialized is phosphoric acid plus a fluorosilicate. Upon reaction you get magnesium hydrogen phosphate; amorphous I emphasize silica; and again the same catalytic role for the HF that forms SiF_6 , which regenerates HF by hydrolyzing the hexafluoride, and recycling the HF (**Figure 23**). The products are shown in **Figure 24**. There is the XRD evidence (**Figure 25**) that indicates that the fluorosulfonic acid completely destroys chrysotile. In this particular picture, the XRD is taken as an additional measure that chrysotile is completely gone. And additional SEM pictures from Bob Sabatini's lab (**Figure 26**) show again the complete destruction of the chrysotile fibers.

But once you have done and understood the chemistry, there is a big jump to go to a commercial process. The traditional thing that you need to do, of course, is to do a pilot plant study of the process in order to scale it up. Where do you do that with a material such as asbestos? We had been very fortunate to have involved the Laboratory safety folks, both within the Department and outside the Department, specifically the Environmental Safety & Health Division, so we had received very good guidance from them from the very beginning. Pat Carr who is in the DAS came up with a terrific suggestion. She said how about using the Inhalation Toxicology Facility (ITF), in the Medical Department. That facility had special permits from EPA and the New York authorities, not to use it to do asbestos in there, but we thought it would do great, if we could get that permit also. That suggestion saved the project, easily I would say, two-years and maybe a couple of million dollars not having to build a new facility. Also, we used that facility very advantageously. W.R. Grace gave us about 3/4 of a million dollars and we put in necessary hoods (**Figure 27**). It is a wonderful facility; HEPA filters, high-efficiency particle absorption; similarly excellent facilities for containing the water, and so on.. I will not describe in any detail here, but it is a unique facility, three rooms, approximately 1200 square feet. I did have to use quite a few of my green stamps with my dear friend Daryl Joel in Medical, but everybody was absolutely terrific, very cooperative. And, this has become a unique facility that allowed us to do engineering operations, e.g. mixing and spraying of asbestos to simulate the fireproofing that exists in buildings; and then to do the actual spraying with the chemicals in this third chamber, for example. So the engineering scale-up was done here at Brookhaven. DOE/EM primarily paid for it, although W.R. Grace put-up quite a bit of money. We had, in addition to the money they

gave the Laboratory, five of their people working full-time at the Laboratory.

We used 34, 3'x3' panels or 3' beams to spray and simulate the fireproofing, which then we treated and we did all kinds of measurements from chemical analysis to release of fibers to acid droplets counts and so on, always having in mind of course that we would have to present all this data to the regulatory agencies. We really strove to have the proper documentation and do things correctly, both scientifically and from a safety standpoint. And, I want to emphasize that we brought in regulatory agencies from the very beginning. Even before the CRADA was signed I went to EPA and their first reaction was ...go away, when you have a process, come back and we'll talk to you. But, we insisted and they worked quite closely with us.

I am summarizing here (**Figure 28**) the tremendous amount of work done in the ITF to show that in the engineering scale phase-up, the work we had done on the bench-scale does work quite effectively. Thirty-four panels and beams were studied. From each one we took 9 cores --each core was sectioned so that we could monitor the depth to which the chemicals penetrated and there were duplicate analyses, by BNL and W.R. Grace; and also there were analyses by XRD both in the laboratories and also at the Light Source; there was Polarized Light Microscopy analyses. **And we were gratified to find that in all samples, with no exemptions, for which the application protocol was followed, the various analyses showed that chrysotile after treatment was less than 1% vs. the 12.7% when we started.** And again I remind you that the regulatory agencies require/consider as asbestos containing material the 1% level. We also made other important measurements.

I will put a viewgraph which is quite busy (**Figure 29**). I apologize for that. Let me draw your attention to 2-3 things that are important. The OSHA PEL (Permissible Emission Level) is 0.1 fiber per cc, and during the engineering scale-up, this is the concentration of the fibers that we measure. And, in fact, if we do different measurements, these are the total fibers and we try to differentiate with TM, which ones are asbestos fibers we show **no fiber production**. That is quite extraordinary, but it's not really surprising. One of the nice innovations, that was a W.R. Grace innovation, although we helped them finesse that, was the way that we apply the chemicals in the commercial process. If you spray, even when you do very gentle atomization spraying, you do generate a significant number, or you could generate a significant number of fibers. And if you exceed the 0.1 fiber level concentration over an eight hour period then you have gained nothing, because you will be obliged to have the plastic cover to create a negative pressure which of course is a most significant part of the overall cost. So, we did apply the foam and the foam even for frayed, mechanically compromised surfaces, the minute it comes into contact with the fibers, they become digested immediately, or if you do generate some fibers, they are taken-up by the foam and they are destroyed. So it is not really surprising that we do have this extremely low level of fiber generation and this is one of the key developments that allows us to cut the cost quite significantly. I will show some cost numbers presently, but I already indicated that 50% of the cost is this negative pressure tenting that low concentrations, given the process obviate the need for this negative pressure. And of course, another very important thing is the acid vapors, especially for HF, for which the regulatory agencies specified 3 parts-per million and again we are way below the particular level.

Let me run very quickly through additional steps in the development. W.R. Grace leased a building, a 50,000 sq. ft. bank in Virginia (**Figure 30**) and they tried-out the process. The results they obtained are in line with what was obtained at the ITF at the Laboratory during the scale-up phase (**Figures 31, 32, 33**). Here we helped them in terms of the protocol, some of the measurements and so on. Also, they did do an Underwriters Laboratory test, actually several tests, and again we helped them with those. Once you digest the asbestos for buildings that you normally would not want to raze, the question arises, is the digested material as effective fireproofing as it was when it was asbestos? That was a very important question, and the answer that we got from UL (Underwriters Laboratory) was a very emphatic yes. In addition, there were animal tests done. These were done at the suggestion of OSHA. And again this shows how important it was that we involved them very early. They (the animal tests) were done through a university. We were not involved in those animal tests at all, They were done by Prof. Oberdoster from the University of Rochester and they were done in Europe. The results, as shown to me by David Myers, came back tremendously good --indicating that there was no adverse pathology associated with the digested asbestos material.

Ok... Let me come towards the end of my talk here. I'm indicating (**Figure 34,35**) some figures relating to cost. Current practice with the site preparation, removal of the fireproofing and so on in this particular study was about \$10-12 dollars compared to the potentially much lower in situ process that we have developed.

According to the terms of the CRADA, W.R. Grace for the Chrysotile had the right to commercialize this in the private sector. There were eight patents issued for chrysotile, 7 to W.R. Grace and one to Brookhaven. So, they are doing the commercialization in the private sector. In August, the first commercial test was done. A New York company, LVI Environmental Services, of New York City received the first license. A number of other asbestos companies are being processed to be licensed by W.R. Grace, I understand (**Figure 36**). According to the terms of the CRADA, we have the possibility, responsibility I would say, of doing a large-scale demo in some DOE facility. We have discussed this with a number of sites, Fernald, Savannah River and Rocky Flats. All have been interested. It appears that this will be done first at Savannah River. We have samples from them. In terms of the amosite, the lesser form of asbestos, that will entail two, perhaps three exclusive BNL patents. And this is very important for thermal insulation. We have just received some money for doing some orientation studies from the U.S. Navy. If that proves useful, I think the Navy is very much interested, but in addition to DOE, EPA, MarketSpan and others expressed a strong interest in this technology.

There are a lot of interesting things that have come out of it but as I conclude I would like to make some general observations. I have listed here (**Figure 37**), what I consider as important lessons learned from this work. And I am positive that carefully structured collaborations do indeed work. We hear a great deal about collaborations, I'm not saying that's the only way to proceed, far from it, however, when properly structured, they can work quite well. And, it can be a win, win, win situation for everyone --satisfying every partner's needs: Peer-reviewed publications and presentations, training of post docs (and we have done this in this particular project), utilization of the Labs facilities (the Light Source was critical); patents have been issued both to the industrial partner and to us; safety, I cannot emphasize this enough, that regulatory agencies be

involved early ... it is a very big plus; a commercial process developed; and of course we did receive some good publicity. Jim Davenport made reference to a very nice statement put out by Secretary Peña (Figure 38); in 1997 he had some nice things to say for us... "Brookhaven Laboratory scientists have helped create an innovative safe solution to attack problem that affects around the country. This is just one example of many achievements at Brookhaven known for its' contributions in medicine, basic research, energy, environmental sciences. Partnerships between Department of Energy's Laboratories and private industry consistently reach tangible rewards. In this case we will make a difference in safely removing asbestos from schools, houses, offices and other buildings", said Mr. Peña.

Let me put up some names (Figure 39). It has been absolutely gratifying to work with a bunch of really wonderful people, under sometimes extremely difficult circumstances. I will not go into that... Marita Allan, Neal Carciello, Dave Elling, Cahit Eylem (a post doc, he's not here anymore), Allen Goland, Joe Hriljac, Jim Hurst, Larry Kukacka, Calvin Lynn, Walter Reams, Bob Sabatini, Toshi Sugama, Ron Webster, Qing Zhu, and a bunch of people from W.R. Grace.

I want to put up one more viewgraph (Figure 40), and I apologize because I'm sure I have not put all the names of all the people that helped in this... at times painful...but extremely satisfying project. Nick Samios personally took a very strong interest in this from the very beginning, as did other people in the Directorate, especially Marty Blume, and Mike Bebon. A few key telephone calls, the ability to use a little bit of the LDRD money, general support .. all those things were extremely good. Peter Bond, in his capacity as Interim Director last year, we are grateful to all for the terrific support. In ES&H, Jeff Williams, Gary Adams, Bob Salvi, Pat Sullivan, Jim Davenport from DAS, a number of people from DAS, Pat Carr, Dr. Krishna, Jim Hurst, the administrative staff, and Gail Brown was the secretary to this project. Plant Engineering were very, very good, especially Raj Yadav did an extraordinary job in renovating the ITF, Technology Transfer people, Peg Bogosian, Mike Furey, they amazed our industrial partners. We were supposed-to-be the slow-step in that interaction. Technology Transfer provided one-hour turn-around time in secrecy agreements. Public Relations, Kara Villamil, Diane Greenburg and others. The Area DOE Area Office, they were absolutely terrific and a number of people in Headquarters and also people at EPA, and OSHA. I thank them all. And, lastly, I thank you for your attention and your interest.

[We have just a few minutes for questions for the speaker...]

Q: Did you have any difficulty in getting penetration of the foam?

A: (LP): No. We worked with 2" thick panels.. W.R. Grace since then have extended that to 3 1/2". You apply the foam, it's amazing it stays in place. I showed you the Channel 12 piece. Over a day, it becomes absorbed, the reaction is slightly exothermic, so you react immediately without really raising the temperature.

Q: What is that?, It looks like you have HF in the front. It may not be what you started with, but.....

A: No.. We looked very carefully at that, it's actually, I tried to indicate, I did not take you through the complete chemistry. It is there. And we monitor that very, very carefully. But, it is recycling, regenerating itself and keeps precipitating out as the fluoride. At no time, once we worked out the protocols did we exceed the 3 parts per million regulatory limit. And that is a very, very important question, because one could take HF acid and do that but we would never had a process.

Q: How do you make the foam?

A: The foam has been primarily a W.R. Grace innovation. Actually, it has been a rather difficult development and it has been critical in terms of limiting the chemicals one can use. But, basically you put in a drum, acid at X%, the water, then you put in a number of binders, and so on , as you might expect the formula is quite complicated, and then simply use air, which you store-up and then you with a spray, very close or very far away you apply that on the surface.

Q: Is the DMA effective on any other asbestos containing materials, such as: aircell pipe leg, or mud-joint packets?

A: Very good question, "Is DMA the Digestion Material for Asbestos effective with other asbestos configurations?".. First of all, let me reemphasize that the DMA that has become commercial is effective only with chrysotile. If you are going to go to other asbestos forms, you'll have to use the BNL technology, number 1... and number 2... there are so many configurations out there that only now this is being developed, for example, the commercial process that was tried out in Connecticut, involved a popcorn ceiling, which had been painted, amazingly enough, it went through the paint, ok... We are negotiating with a utility company they have, there are thousands even for this, tens-of-thousand, even for this utility company valves which have been insulated with some asbestos containing concoction that we have not really tried. The first results from some tile...even though that is a very tight material and so on, they appear promising. So, we don't know yet to what extent, but that is something that is being worked on and there are some very extremely encouraging developments.

Q: You mean floor tile, or ceiling tile?

A: It doesn't make any difference... because the foam will stay..

Q: Will it penetrate vinyl asbestos floor tile?

A: That we don't know. I personally doubt that, we havn't tried that, and to my knowledge, W.R. Grace has not penetrated that. No.

Q: Isn't this a potentially awfully hazardous for the applicators?

A: That as you might suspect, was a question that we paid close attention to... again, the question is.... Will that be potentially dangerous for the applicators? We monitored very, very closely the ambient environment. The reason the engineering scale-up was done at the ITF, why the ITF was an ideal place, is that it allowed us to do this experiments in an enclosed place, but we did that as if...well, it was enclosed, but we were monitoring to see whether we would have measurements that would allow us not to have the enclosure. The fiber concentration was so low in all cases that is really no problem, ok? The concentration fiber has been at least one order of magnitude and often 2 orders of magnitude below the limit. The hazard that you face, potentially is from the acids. HF, we have eliminated, it is again below... so, any protection would have to be involved, would have to be protection for acids.

LP: "Steve?.."

Q: You commented about the 1%, which is the, triggers the concern of this as a hazardous material, to which I am infer that it's 1.01% spacesuits are required and 0.09% that its' no hazard what-so-ever.. Which I guess you have to draw a line someplace and that's where the line's been drawn. So, but that don't... you started off with one of your viewgraphs had a 12.7% as your starting material, so... in principle you're really trying to get down in order of magnitude and then in some sense, you're done. How far do you get? Do you get an order of magnitude?

A: I can show some data Steve.. Some real data.. Let me see what I can get my hands on quickly.. That at times.. Here is XRD the analysis.. I don't know whether you can read them.. This is from the field test and this was 0.6, 0.3, .3, .3, 0, and so on.. The low was 0 the high was .81, here's the mean and the median. So..

Q: Those the actuals ?

A: These are the actual figures, yes. From one of the many tests, so.. This was a very, very sensitive point, along with HF and the fiber count. We payed a great deal of attention to. Now, why the 1%, as you said, somebody will have to... you'll have to draw the line somewhere, this is where EPA and OSHA have drawn the line.

["How about two more questions from over here"]...

Q: Again, you're eluding that asbestos that's there now, if one doesn't do anything with it, it's harmless?

A: If it is not in the air...

Q: So, why are you spending a-hundred billion dollars, and why is it all this To clean up....? And I think I know the answer

A: The regulatory agency position is that, if it exceeds 0.1 fiber per cc, average over an 8-hour period, you as the building owner, you have a problem and you must do something about it. And if it is not in the air. And the same with material asbestos that is being, not inhaled, but taken in.. Please...

(Audience asks question...LP repeats the question....)

Q: Good question....What do we do with residual sulfuric acid or any of the other acids?

A: Two things, one look very carefully to monitor and determine the uptake. Before you do a job, the first thing you do, you get cores from the floor or the ceiling, whatever to determine how much there is and then you work from there and you try to do the stoichiometry. The W.R. Grace people in the field have added a food dye that tells you when you have — changes color when you have done, destroyed completely the asbestos, but in case there is some residual acid, they do paint over it to neutralize it. There is, they have added potentially a neutralization step.

Q: (Can't hear it, sorry)...

A: Some mild soda-bicarbonate, something like that, something very mild... I guess our Chair says...

Chair: Yeah, if there's any more questions, we can continue afterward at the reception and I think we should thank the speaker one more time.

Applause...

Newsday

EDITORIALS

"Where there is no vision, the people perish."

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Brookhaven Breakthrough

By solving the asbestos disposal problem, the national lab proves again its value

Asbestos, once thought of as a wonder insulator, is also a deadly carcinogen, dangerous to disturb and costly to remove. That could change early in the new year as W.R. Grace & Co. moves a new product -- perfected at Long Island's Brookhaven National Laboratory -- to market. The breakthrough could not have come at a better time for the embattled federal facility. It adds new luster to the reputation of the laboratory, which -- despite recent attempts to transform it into a political football -- is a regional treasure.

The new product is a foam spray that leaches into asbestos and transforms it from dangerous dustiness into an inert, nonfibrous, fireproof material. W.R. Grace researchers sought the collaboration with the national laboratory.

It's ironic: Sen. Alfonse D'Amato (R-N.Y.) and Rep. Michael Forbes (R-Quogue), demand closure of Brookhaven's nuclear reactor, contending it contaminates the environment. With this asbestos palliative, the lab has come up with the answer to one of the nation's

most serious environmental problems.

The controversy erupted last Jan when Suffolk health officials noted a plume of industrial solvents, not radioactive and necessarily from the laboratory, moving under an area of North Shirley. Faced with current charges of environmental laxity at the laboratory, the Department of Energy offered to pay to connect residents of the area to the public water system. When a plume of radioactive tritium was detected under the lab, Energy Secretary Federico Pena fired the lab's top managers and later named a new management headed by physicist John Marburger, former president of the State University of New York at Stony Brook.

Sniffing demagogic opportunity, D'Amato and Forbes first demanded an investigation by the Energy Department's inspector general and then sought closure of the reactor.

Recently, addressing the reactor's future, Marburger said: "We need to convince ourselves we can run it without any more spills, accidents or danger to the environment." He should get the chance to do just that.

FIGURE 1

A Channel 12 Video

FIGURE 2

ASBESTOS

ἄσβεστος

A = non

σβέννυμι = to extinguish

"inextinguishable" (euphemistic)

First mentioned by Aristotle's
student Theophrastos in the text
ON STONES

FIGURE 3

Brooklyn School Races To Clean Out Asbestos

Late Discovery Imperils Thursday Opening

By JOE SEXTON

Asbestos-removal workers moved from room to room last week inside Public School 181 in Flatbush. Construction workers shouted orders. Officials ranging from the school's principal to School Construction Authority executives to teachers' union representatives met behind closed doors to talk about air-quality measurements and contingency plans.

The race was on at the Brooklyn elementary school, a race against chaos school officials say was spawned by a rebuilding project.

On Thursday, 1,100 kindergartners through fifth graders are expected to show up at P.S. 181 in District 17. The hope is that the asbestos readings will be safe, that the classrooms will be clean. If not, almost everyone involved agrees with worried, embarrassed shrugs, there is no telling what will happen.

"You say to yourself, maybe we will have to bus the children elsewhere," said Gertrude Erwin, the principal of P.S. 181. "But then you realize that District 17 is one of the most overcrowded in Brooklyn. There is no place to bus them. The people from the School Construction Authority have said they will have this school ready. But as I've been saying to people: light a candle."

P.S. 181 is in the third year of a \$33 million overhaul that includes the addition of a new building. The asbestos problem began to take shape in early August. School Construction Authority officials say the contractor renovating the 88,000-square-foot main school building began to replace the building's windows but failed to take precautions against possible asbestos contamination.

John Raneri, the project manager for the contractor, Gemma Construction of Hicksville, L.I., said from the site over the weekend that the window removal was done in accordance with the contract. "If they say something is a hot area, we treat it as a hot area," he said. "They didn't say anything."

Soon after work on the windows began, officials discovered that the concrete floors throughout the main building, a five-story structure built in 1924, were contaminated, as were the windows. Worse, the new annex, where the bulk of the school's pupils

Thursday.

They said that air-quality readings in the annex were safe, and that more would be taken before classes begin. The limited portion of the main building that the school was going to use this year — the first floor and 11 classrooms adjacent to the annex — had been cleaned, they said, and the rest of the contaminated floors and rooms had been contained. They said construction crews were working 24-hour shifts through the weekend to finish the work on the annex.

"What happened, finding the asbestos in the floors, is very rare," said Doris Gonzalez-Light, director of external affairs for the School Construction Authority. "But this

'Finding the asbestos in the floors is very rare.'

school will be ready. It will be done. It has to be."

JoAnne Carlie, the president of the parents' association, was not so optimistic last week. "I will not allow children in that school unless it is healthy — not only physically healthy but healthy enough for children to be properly educated in it," she said.

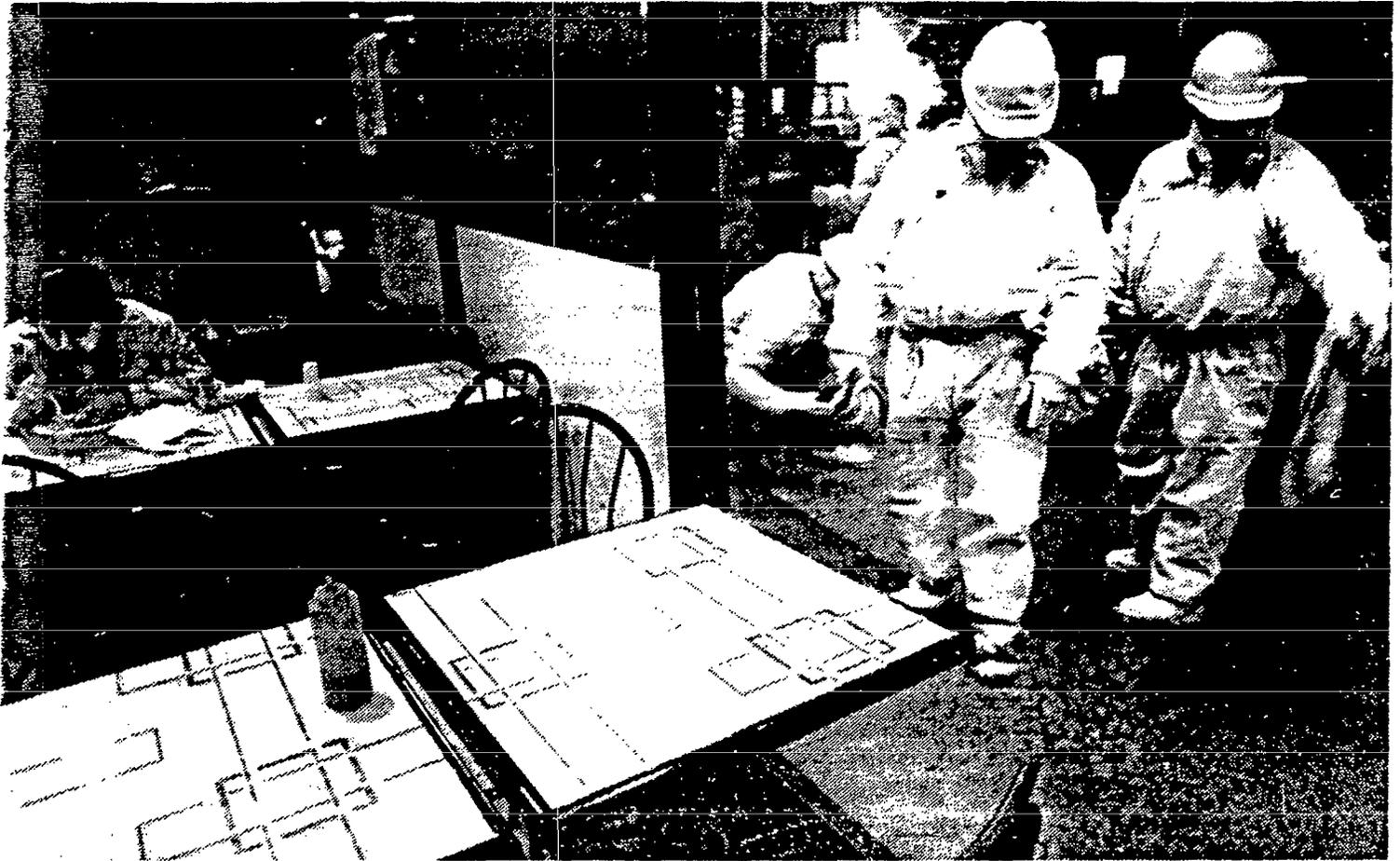
Construction trailers lined the street in front of the school on New York Avenue last week. Classrooms in the annex were unfinished last week and furniture was stacked to the ceilings.

Although teachers are scheduled to report on Tuesday to put their classrooms in order, several who were getting a headstart wheeled books and supplies over plywood bridges and feigned smiles.

"Grim, just grim," said Shirley McIntosh, who is beginning her sixth year as a teacher at the school.

Two years ago, at the height of the asbestos crisis that delayed the opening of many city schools, the fifth grade at P.S. 181 was transported to the Community School District Office for classes. But Barbara Byrd-Bennett, the administrator appointed last winter to replace the

FIGURE 4



Linda Rosier for The New York Times

unrelated failures of the city's infrastructure crippled the East Side yesterday. A woman eats lunch at the Hoo Won Express restaurant, on the corner of East 56th and Lexington Avenue, seemingly oblivious to the crew of asbestos-removal workers cleaning the sidewalk outside.

First a Steam Pipe, Then a Water Main, Then Tempers

Continued From Page B1

he said. Michael Cha, the manager of a restaurant in the building, said the messengers for his walk-in freezer were under water. "It's going to be closed for a long time," he said of the restaurant.

Gelber said that the flooded section was a major subterranean hub, with two 48-inch mains, two 36-inch mains, one 36-inch main and one 10-inch main crisscrossing the block. Figuring out which one was ruptured took some time, but within an hour after the water surged

to the surface, she said she believed that the problem was with the 36-inch main and that it had been shut off.

"The larger the break, the longer it takes to shut it down," she said.

Con Edison said within 90 minutes of the steam-pipe leak that asbestos had been released, though the utility could not say how much had been sprayed through the densely populated neighborhood of apartments and office buildings. The asbestos had been used in a sleeve-like wrapping for the pipe, which Con Edison officials said had been laid in 1964.

Ms. Gelber said that Con Edison "appears to be moving with good speed" toward cleaning up the area.

Two more failures of the city's creaky infrastructure.

As workers in contamination-resistant suits swarmed on their hands and knees, scouring bits of asbestos from the pavement with small brushes, Ms. Gelber said she saw no reason the closed streets could not be reopened in time for this morning's rush.

"The concern is to move quickly

with the cleanup to avoid people tracking it all over the area," she said.

And the steam drew lunch-hour crowds of gawkers. Big-name partners from law firms looked down from their windows while paralegals took the elevator to the street. Dan Callahue, who works in an office building at Third Avenue and 56th Street, said that he saw the steam rising while sitting in his office on the sixth floor.

The disruptions caused havoc for traffic in midtown Manhattan, and tie-ups continued last night well past the rush hour.

FIGURE 4A

NIE Plusieurs organisations sectorielles de la santé dénoncent prochainement « épidémie » de cancers imputables à l'exposition, durant les années 60 et 70, à

l'amiante. Elles assurent que l'on pourrait compter 100 000 à 150 000 décès en France dans les vingt prochaines années. ● AU-DELÀ de la querelle de chiffres sur le nombre

de décès consécutifs à une exposition à l'amiante, la progression des cas de cancer du péritoine ou de la plèvre est incontestable. ● ISOLANT thermique très efficace, l'amiante a

été très largement utilisée dans l'industrie, du bâtiment avant d'être sévèrement réglementée et, dans certains pays, totalement bannie. ● LES ASSOCIATIONS exigent des

pouvoirs publics un général des bâtiments l'interdiction de l'amiante encore en France dans une douzaine d'usines.

Le Monde 31-5-95

Le nombre de cancers dus à l'amiante menace de se multiplier

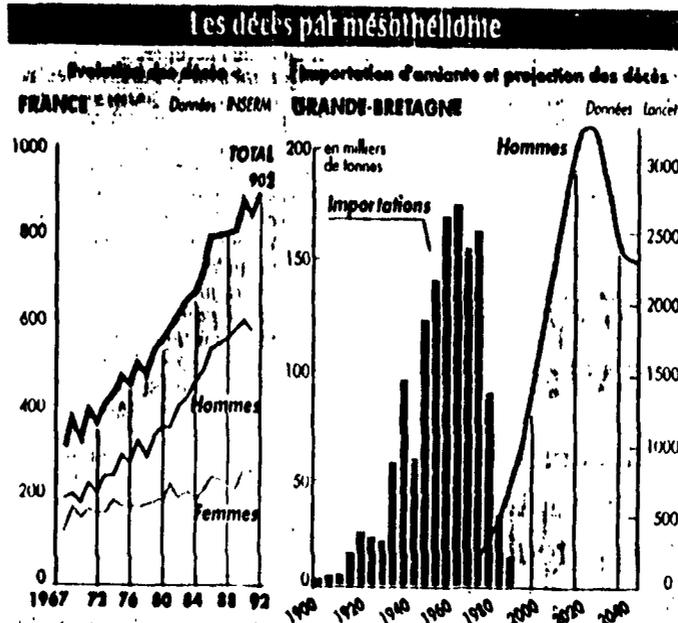
Plusieurs associations et spécialistes estiment que l'exposition à cet isolant, interdit dans plusieurs pays européens, pourrait provoquer plus de cent mille décès dans les vingt prochaines années

Plus de cent cinquante personnes pourraient mourir au cours des vingt prochaines années des suites d'un cancer provoqué par une exposition à l'amiante pendant les années 60 et 70, est du moins ce que craignent un nombre d'associations et de la Fédération nationale des syndicats du travail et des handicapés (Fnath), la Mutualité française, la Ligue contre le cancer et l'Association pour l'étude des cancers du travail (Alert), qui se réuniront, mardi 10 mai, à Paris, en conférence de presse. « On s'attend à une véritable épidémie », précise Marcel Royez, secrétaire général de la Fnath. Les décès dus aux différents cancers provoqués par l'amiante sont estimés à 10 000 à 20 000 morts entre 2015 et 2020. Soit au moins les accidents mortels de la

aujourd'hui en France. Un chiffre qui « ne peut pas manquer d'impressionner », indique-t-on au ministère de la santé. Un chiffre que conteste cependant le professeur Jean Bignon, du Comité permanent amiante (CPA) — une structure mise en place en 1982 par les industriels de l'amiante et à laquelle les pouvoirs publics participent —, qui considère que « 70 % des mésothéliomes échappent à l'amiante ».

Quelle que soit l'hypothèse retenue et la part faite aux sous-estimations ou aux surestimations, cette querelle de chiffres ne saurait masquer l'incontestable progression de ce cancer, dont la particularité réside dans un temps de latence extrêmement long : le mésothéliome se déclare trente à cinquante ans après une première exposition. L'usage de l'amiante comme isolant thermique s'est largement répandu à partir des années 60 avant d'être sévèrement réglementé, principalement sous l'influence de la Communauté européenne (fixation de valeurs limites en 1977, interdiction des amphiboles — la variété d'amiante la plus dangereuse — en juillet 1994). C'est donc à partir de maintenant, jusqu'à un « pic » atteint vers 2015 ou 2020, que les cancers vont se déclarer.

L'épidémie risque d'être d'autant



La situation en Grande-Bretagne est largement comparable à celle de la France. Le décalage entre les deux courbes provient du temps de latence de déclaration des cancers après l'exposition à l'amiante.

France, selon les calculs de l'Alert, à un total de l'ordre de 3 000 cancers mortels provoqués par l'amiante. Un chiffre considérable, qu'aucune statistique officielle ne confirme : seule une soixantaine de mésothéliomes sont reconnus

devrait se mettre en place prochainement sous l'égide de l'Inserm. A la direction générale de la santé (DGES), où on chiffre prudemment les cas de mésothéliomes « entre 500 et 1 000 », « personne ne

personnes vivant dans l'environnement des usines productrices. Il faut ajouter les ouvriers qui ont procédé au flocage à l'amiante des structures métalliques des bâtiments, procédé très répandu, de la fin des années 50 jusqu'à son interdiction en 1978 ; les ouvriers d'entretien — électriciens, câbleurs, plombiers — qui continuent de travailler à la maintenance d'édifices dont on ignore souvent s'ils contiennent de l'amiante ou de la laine de verre ; et les personnes qui vivent dans des immeubles floqués (6 000 à 12 000 selon Alert) et qui, selon la DGES, ne courent pas de danger sauf en cas de pic d'exposition sporadique accidentel.

Afin de limiter l'ampleur de l'épidémie, les associations exigent des pouvoirs publics qu'ils sortent de leurs atermoiements et qu'ils bannissent définitivement l'amiante en France. Car, contrairement à d'autres pays européens, on compte encore une demi douzaine d'usines d'amiante sur le territoire français (Saint Gobain est le troisième producteur mondial). Une autre mesure consisterait à entreprendre d'urgence un recensement général des immeubles floqués à l'amiante. Des halles de Rungis à l'aérogare de Bastia, du centre de tri Saint-Lazare au lycée d'Haumont, du CHU de Clermont-Fer-

s'opérer à partir de place ». Il faut donc agir au cas par cas de manière « élémentaire », considérant que « indispensable », estime Bignon, « raisonnement CPA. Seul le ministre juge cet inventaire dans la mesure où de réalisation (absolument sible dans plusieurs (lire ci-contre) ne le France ?

Un matériau

- **Propriétés.** L'amiante, matériau naturel de caractéristiques est d'excellentes propriétés de résistance au feu. L'amiante est le chrysotile. Les autres variétés sont des amphiboles (crocidolite et amosite). Depuis 1994 en France, l'usage de l'amiante est interdit.
- **Industrie.** L'industrie transformatrice utilise l'amiante dans les produits de construction, les joints, des garnitures, etc.

FIGURE 5

La réglementation en Europe

Sept pays européens ont procédé à l'interdiction totale de l'amiante : l'Allemagne, les Pays-Bas, l'Italie, la Suisse, le Danemark, la Suède et la Norvège. Des inventaires de tous les bâtiments sus-

amment amiante, afin d'arrêter tout usage résiduel de l'amiante et

ASBESTOS "MAGIC" MINERAL ARTICLES

- **Woven Articles** Cloaks, Tablecloths, Theater Curtains, Fireprotection Suits, Gloves, Shrouds
- **Insulation** Fireproofing of buildings and ships; thermal insulation of pipes
- **Automobiles** Brake and clutch linings
- **Filters** Cigarettes, Hospital ventilations, military gas masks, fruit juice & wine
- **Building materials** Roofing, Flooring (vinyl asbestos)
- **Military** Parachute flares, Bazooka shells and torpedos and surgical dressings
- **Miscellaneous** Buttons, telephones, toothpaste
- **"Asbestos Man"** Johns Mansville exhibit at the 1939 NY World's Fair

HEALTH IMPLICATIONS

- 100 A.D. **Pliny the Younger comments on diseases of asbestos workers**
- 1890-1895 **High death rates among French and English asbestos weaving/cording Asbestos workers**
- 1927 **Complete description of ASBESTOSIS (non-malignant scarring of lung tissue)**
- 1936 **Relationship between asbestos dust exposure and BRONCHIAL CARCINOMA.**
- 1960 **MESOTHELIOMA, exceptionally rare in the general public, mostly found among asbestos workers. Cancer of the linings of thoracic or more rarely of abdominal cavities (peritonium). Amphiboles seem to be implicated along with respirable (<1 nm diameter) fibers. Cigarette smoking synergism.**
- A number of benign pleural changes (effusions, fibrosis)**

FIGURE 7

- **Peak Production** ~ 5×10^6 Metric tons/year

[90% Chrysotile]

- **Atmospheric Concentration**

- **10-100 ng/m³**
- **5×10^3 ng/m³ near factories**

- **Regulatory Agencies (EPA, OSHA)**

- **PEL 0.1 fiber/cc**
- **ACM ≥ 1 wt%**

FIGURE 7A

AMPHIBOLES [SiO₄ Chain Structures]

- **AMOSITE**
 - Brown Asbestos
 - Refractive Index 1.55 - 1.64
 - (Fe⁺² Mg)₇ Si₈ O₂₂ (OH)₂

- **CROCIDOLITE**
 - Blue Asbestos
 - Refractive Index 1.69 - 1.71
 - Na₂ Fe₂⁺³ (Fe⁺² Mg)₃ Si₈ O₂₂ (OH)₂

SERPENTINES [Layered Silicate Structures]

- **CHRYBOTILE**
 - White Asbestos
 - Refractive Index 1.50 - 1.57
 - Mg₃ (Si₂ O₅) (OH)₄

FIGURE 8

	SiO₂	FeO	MgO
Chrysotile	39	~1	38
Amosite	49	41	7

FIGURE 9

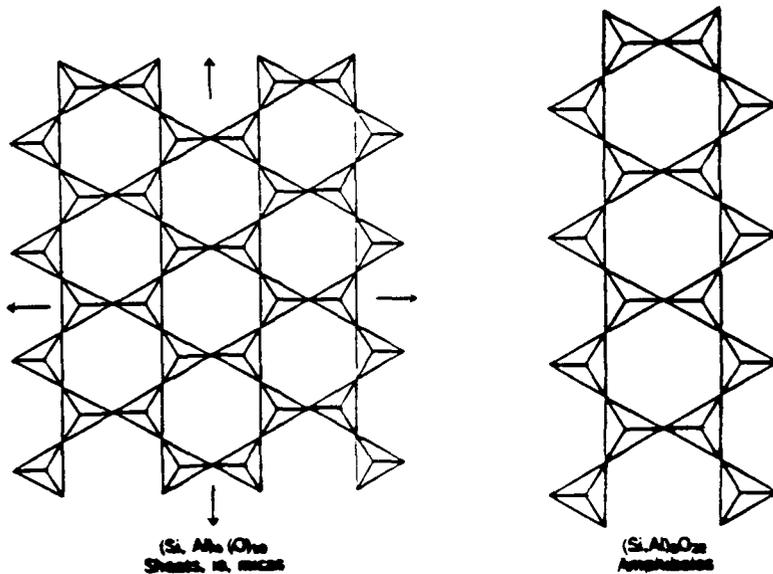


Fig. 3. Silicate backbones of chrysotile and amphiboles: (a) the sheet silicate structure of chrysotile, analogous to that of micas; (b) the double-chain silicate structure found in amphiboles (12). Courtesy of Oxford University Press.

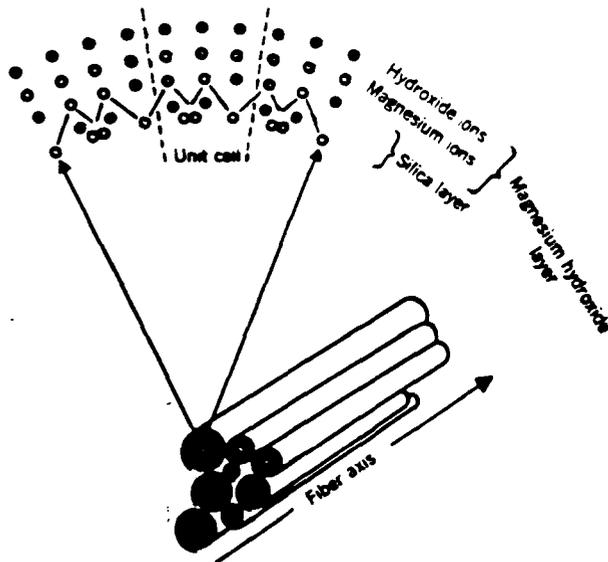


Fig. 4. Microscopic structure of chrysotile fibers (10). Reprinted with permission.

067

Kirk-Othmer

FIGURE 10

Asbestos Digestion Project

Chemical Composition:
 $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$

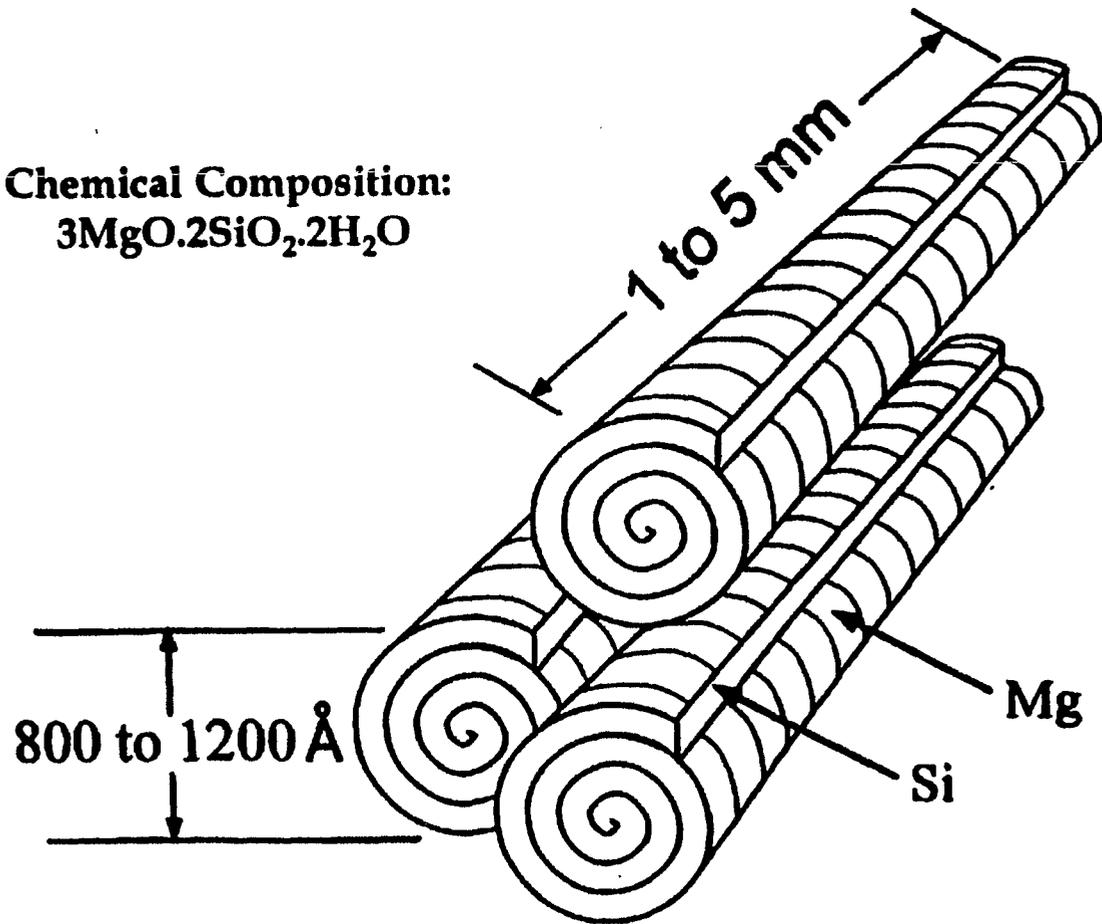


FIGURE 10A

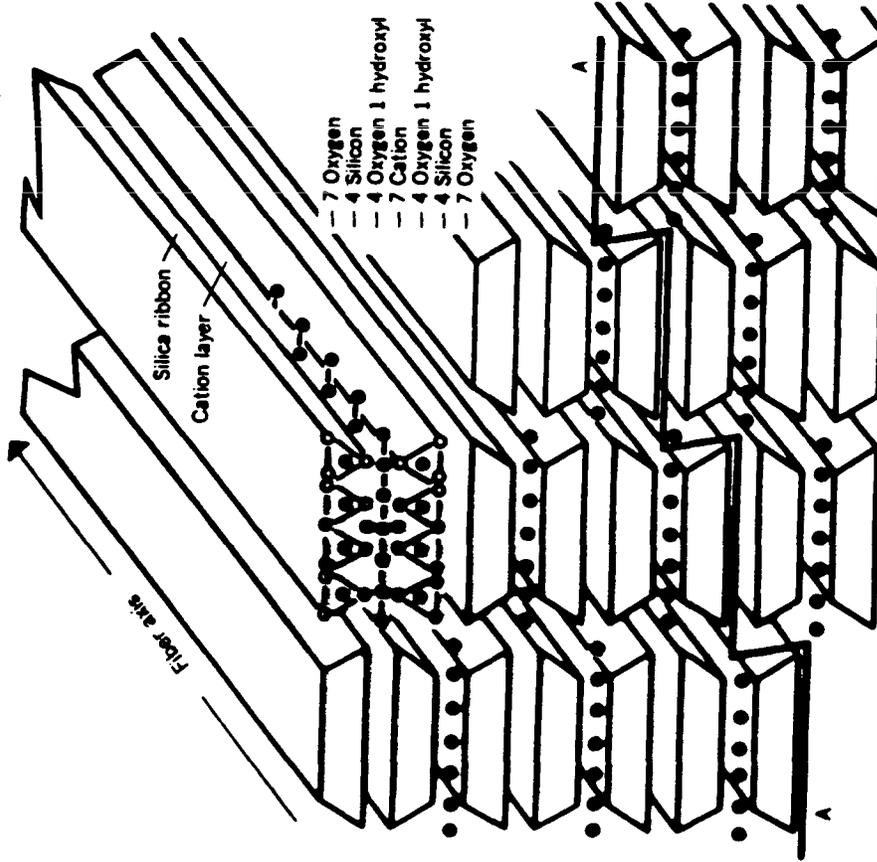


Fig. 5. Microscopic structure of amphibole fibers (10). Reprinted with permission.

Kirk-Othmer

FIGURE 10B

SUPERACIDS

[Brönsted Acid + Fluorinated Lewis Acid]

[Acidity > 100% H_2SO_4]

<u>Acid</u>	<u>H_a</u>
H_2SO_4	-12 (Std)
$\text{H}_3\text{PO}_4 - \text{BF}_3$	-19
HSO_3F	
$\text{HSO}_3\text{F} - \text{SbF}_5$	
$\text{HF} - \text{SbF}_5$	

FIGURE 11

Patent 5,763,738 (6/9/98) (Sugama & Petrakis)

**Chemical Agents for Conversion of Chrysotile Asbestos
into Non-Hazardous Materials**

FSO₃H [Fluorosulfonic]

F P(O) (OH)₂ Fluorophosphoric

HF₄ Fluoroboric

H₂Si F₆ Fluorosilicic

FCH₂CO OH Fluoroacidic

F C₆ H₄ CO OH Fluorobenzoic

CF₃ SO₃ H

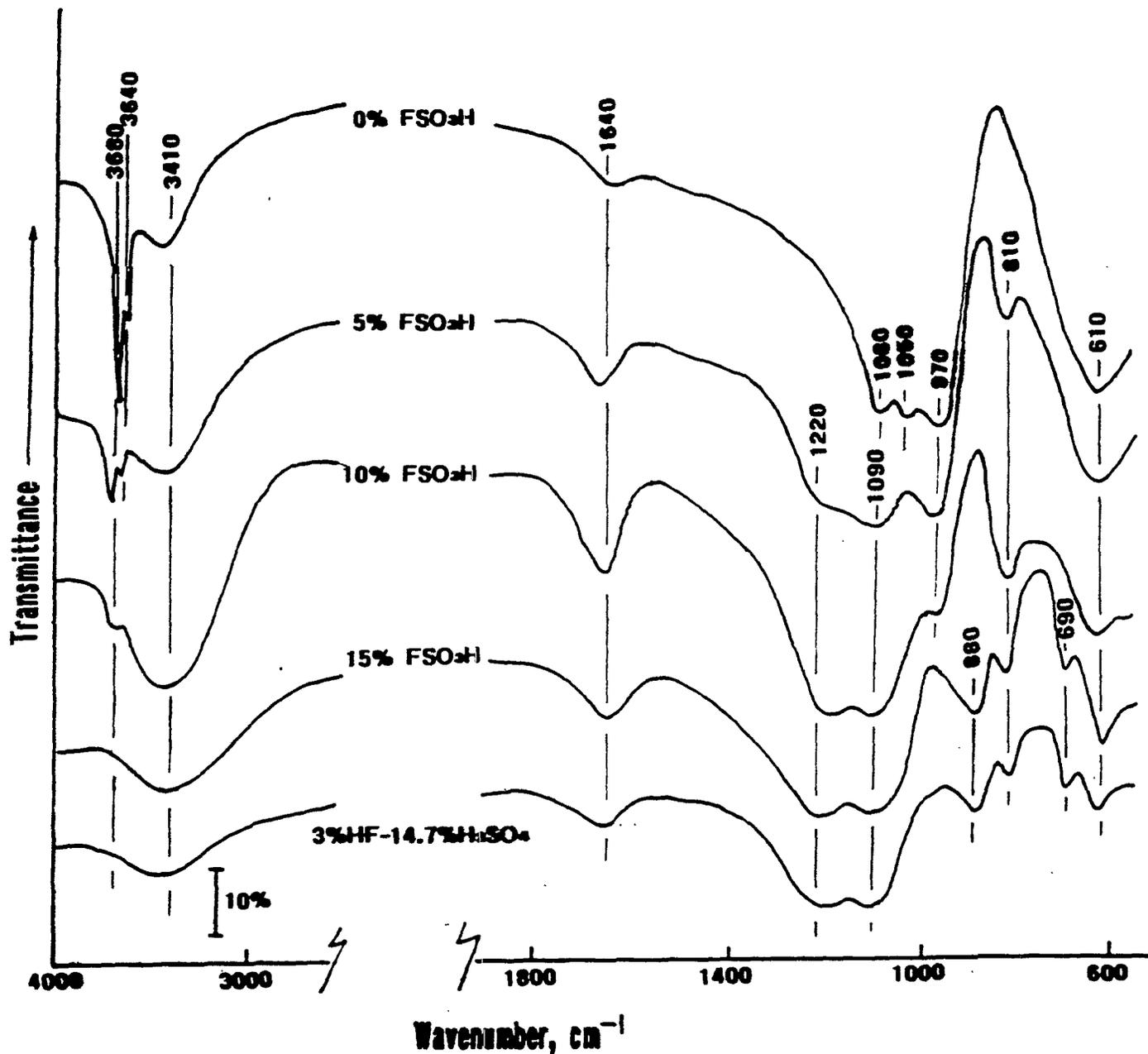
C₂ F₅ SO₃ H

C₅ F₁₁ SO₃ H

C₈ F₁₇ SO₃ H

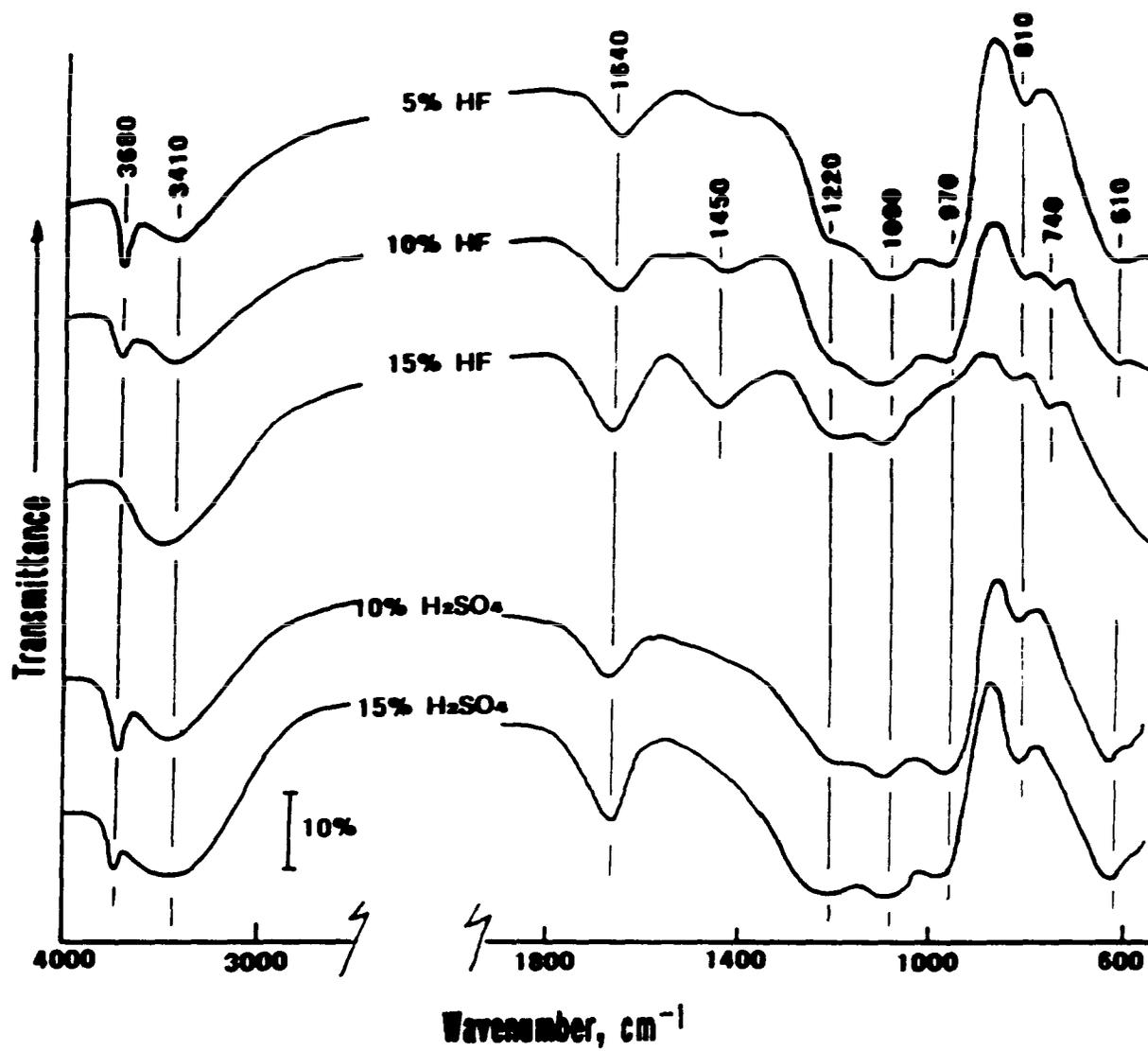
FIGURE 12

FIGURE 13



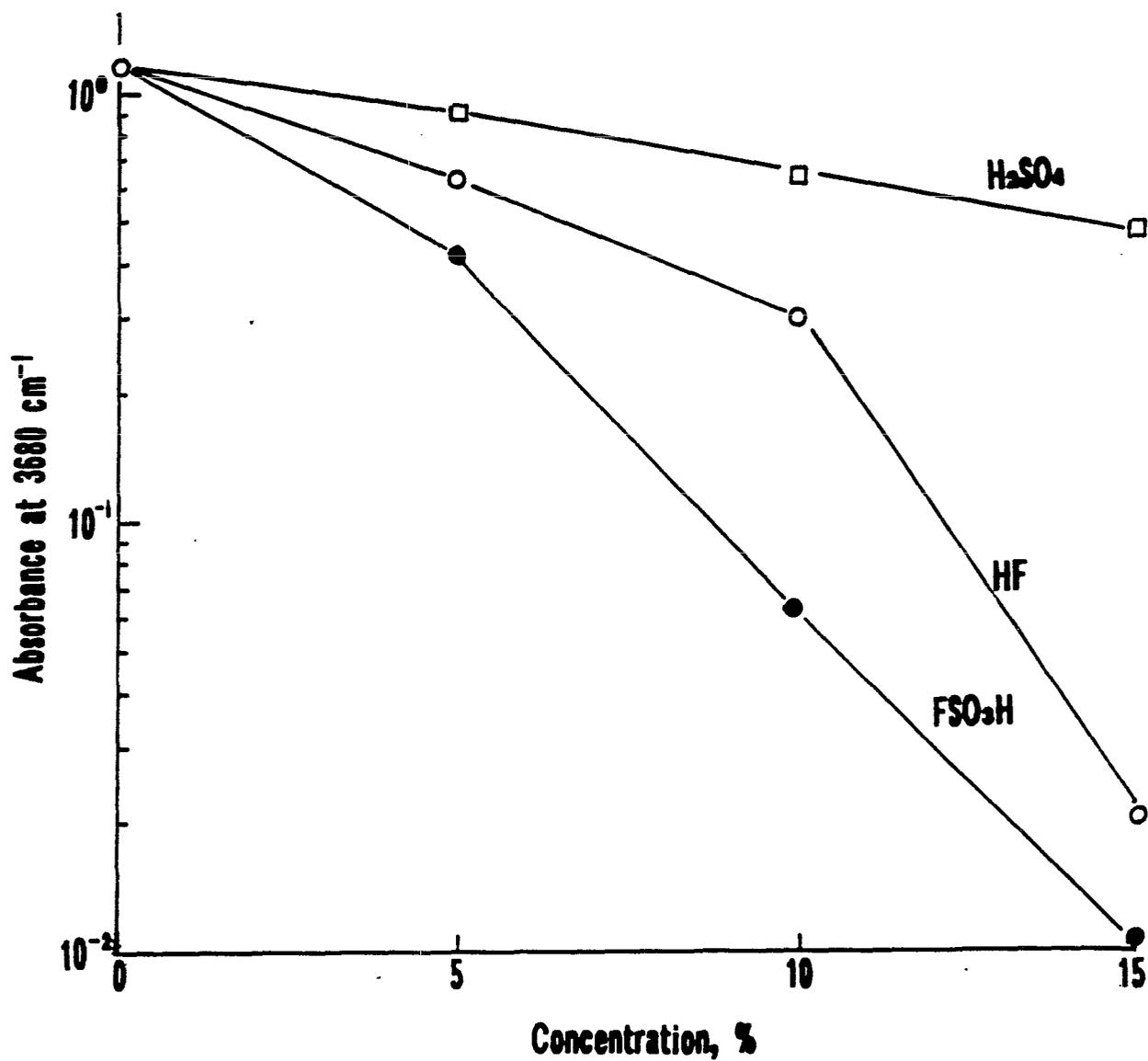
FT-IR absorption spectra for the 0, 5, 10, and 15 wt% FSO₃H-treated chrysotile asbestos samples, and the asbestos sample treated with a 3 wt% HF-14.7 wt% H₂SO₄ solution, corresponding to the equilibrium relation of 15 wt% FSO₃H in aqueous medium.

FIGURE 14



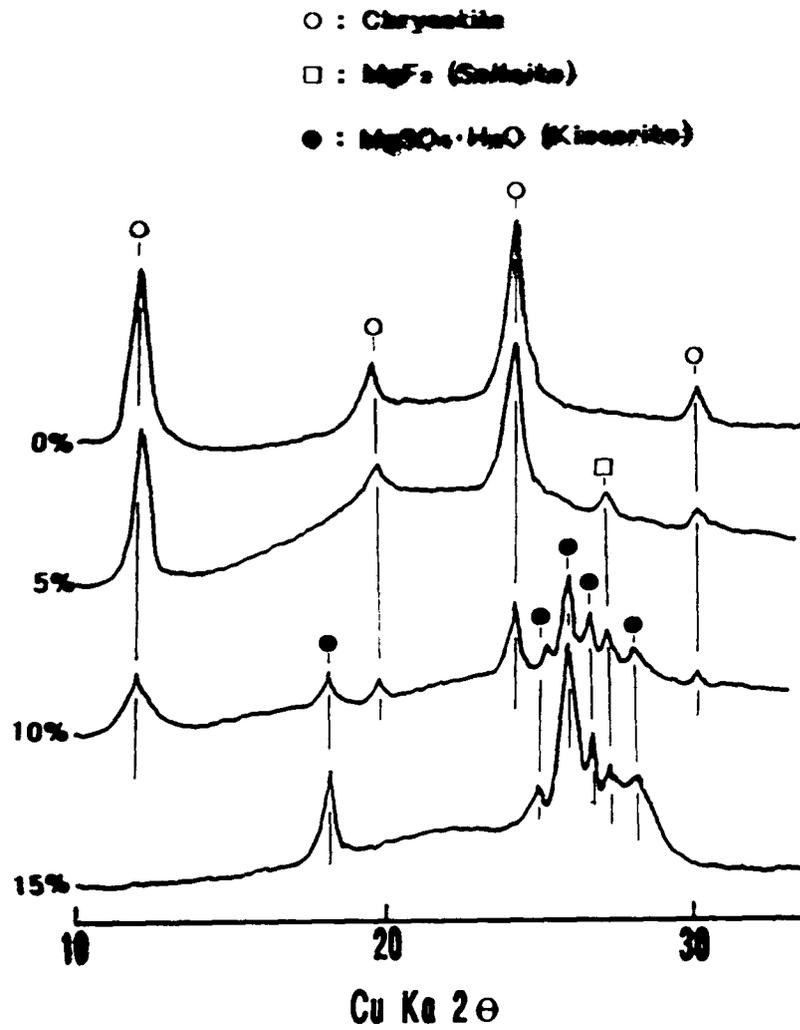
FT-IR spectra for 5, 10, and 15 wt% HF- and 10 and 15 wt% H_2SO_4 -treated fibers.

FIGURE 15



Changes in absorbance at 3680 cm⁻¹ for the FSO₃H-, HF-, and H₂SO₄-treated asbestos fibers as a function of concentration of chemical reagents.

FIGURE 16



Comparison between XRD patterns for 0, 5, 10, and 15 wt% FSO_3H -treated chrysotile asbestos.

FIGURE 17

CHRYSOTILE- FLUOROSULFONIC ACID

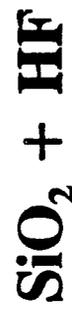
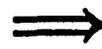


FIGURE 18

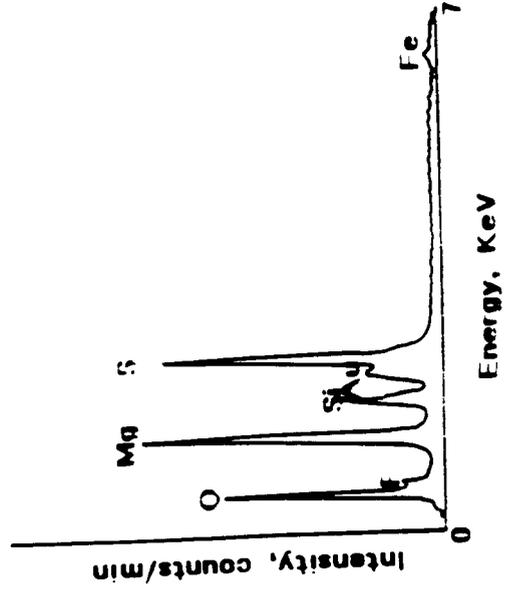
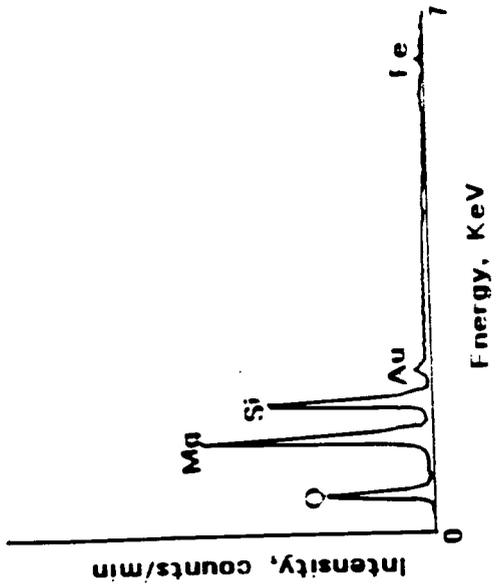


FIGURE 19

(Not shown.)

A Light Source Beam Line

FIGURE 20

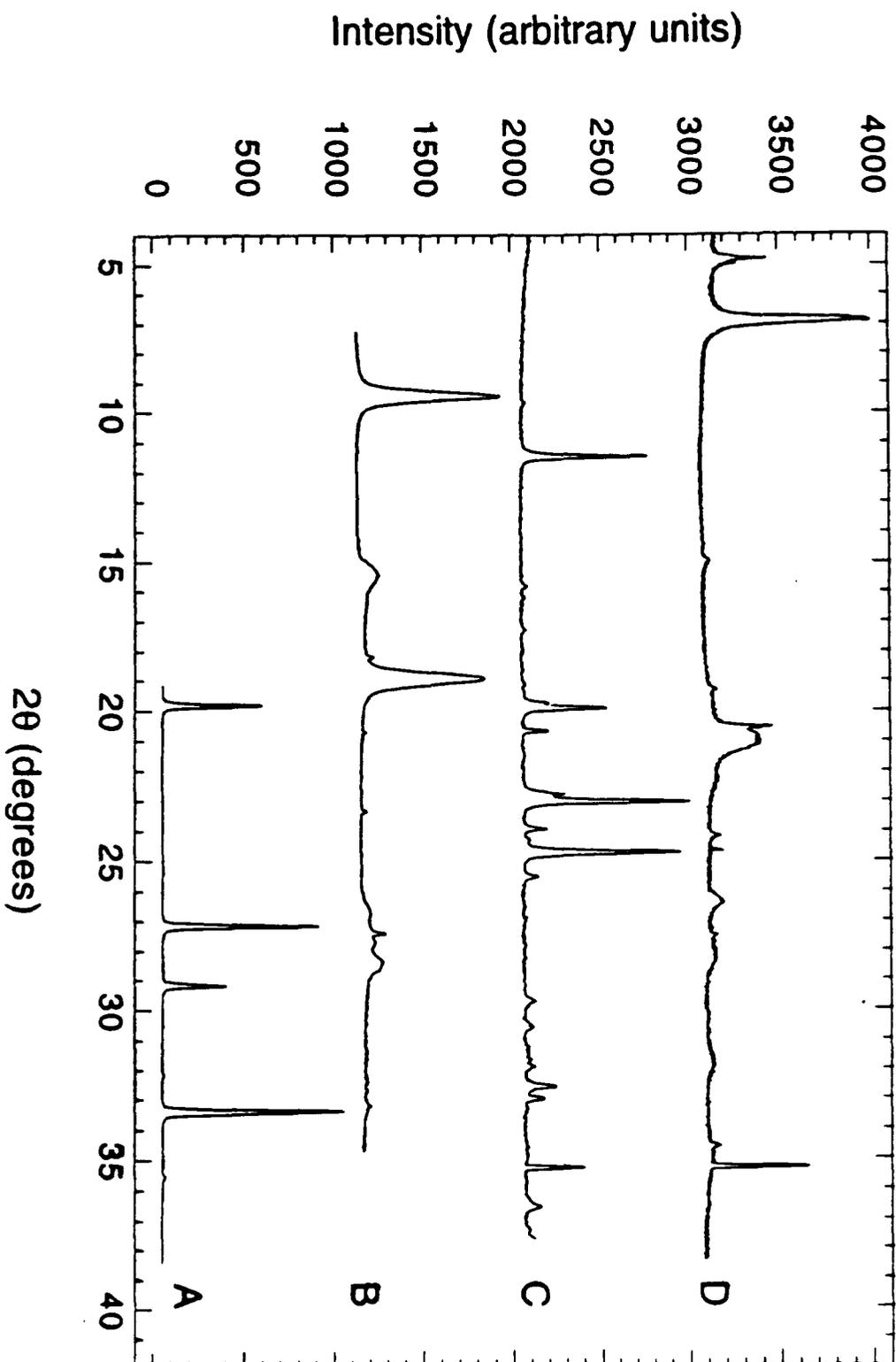


FIGURE 21

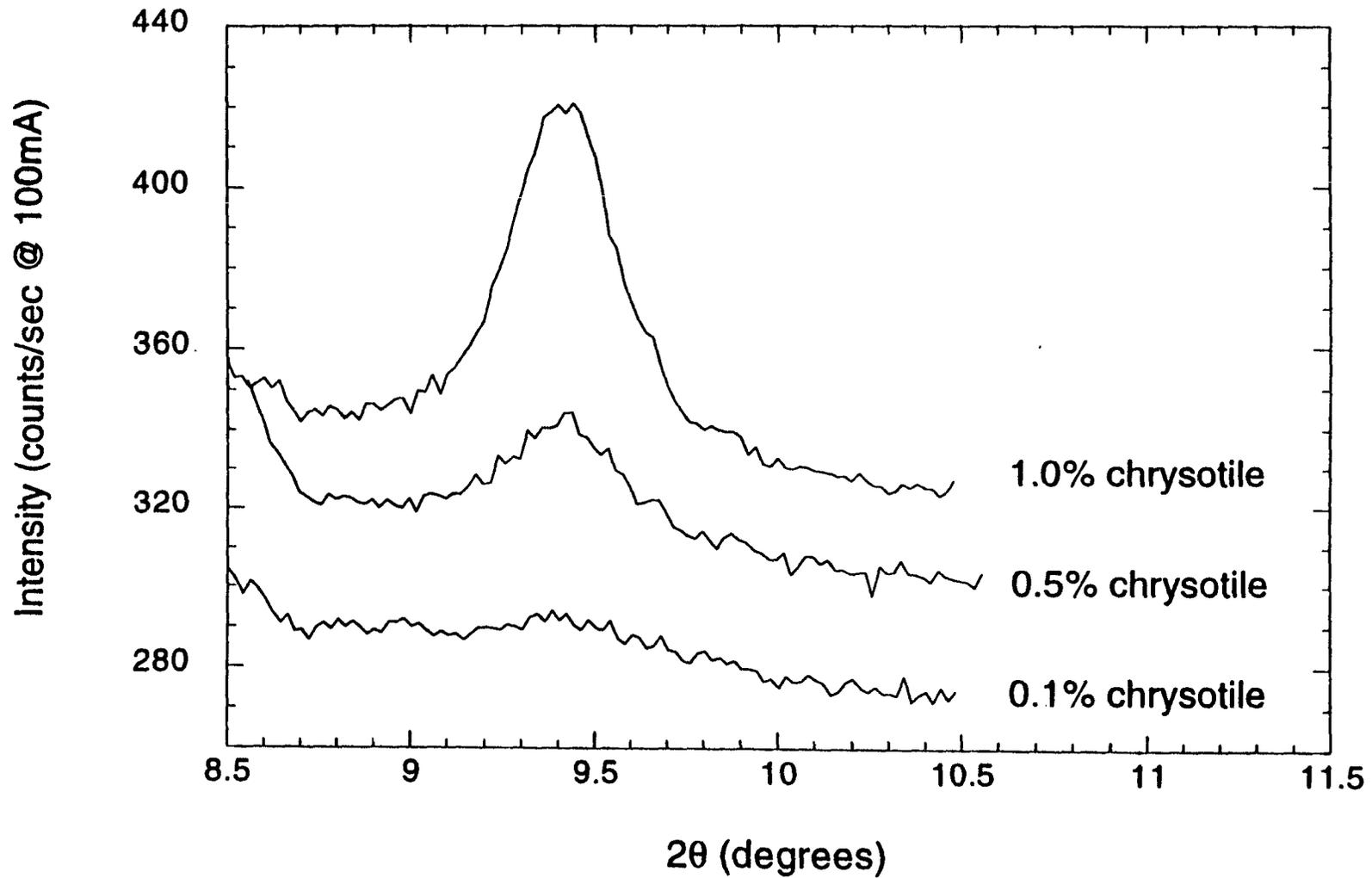
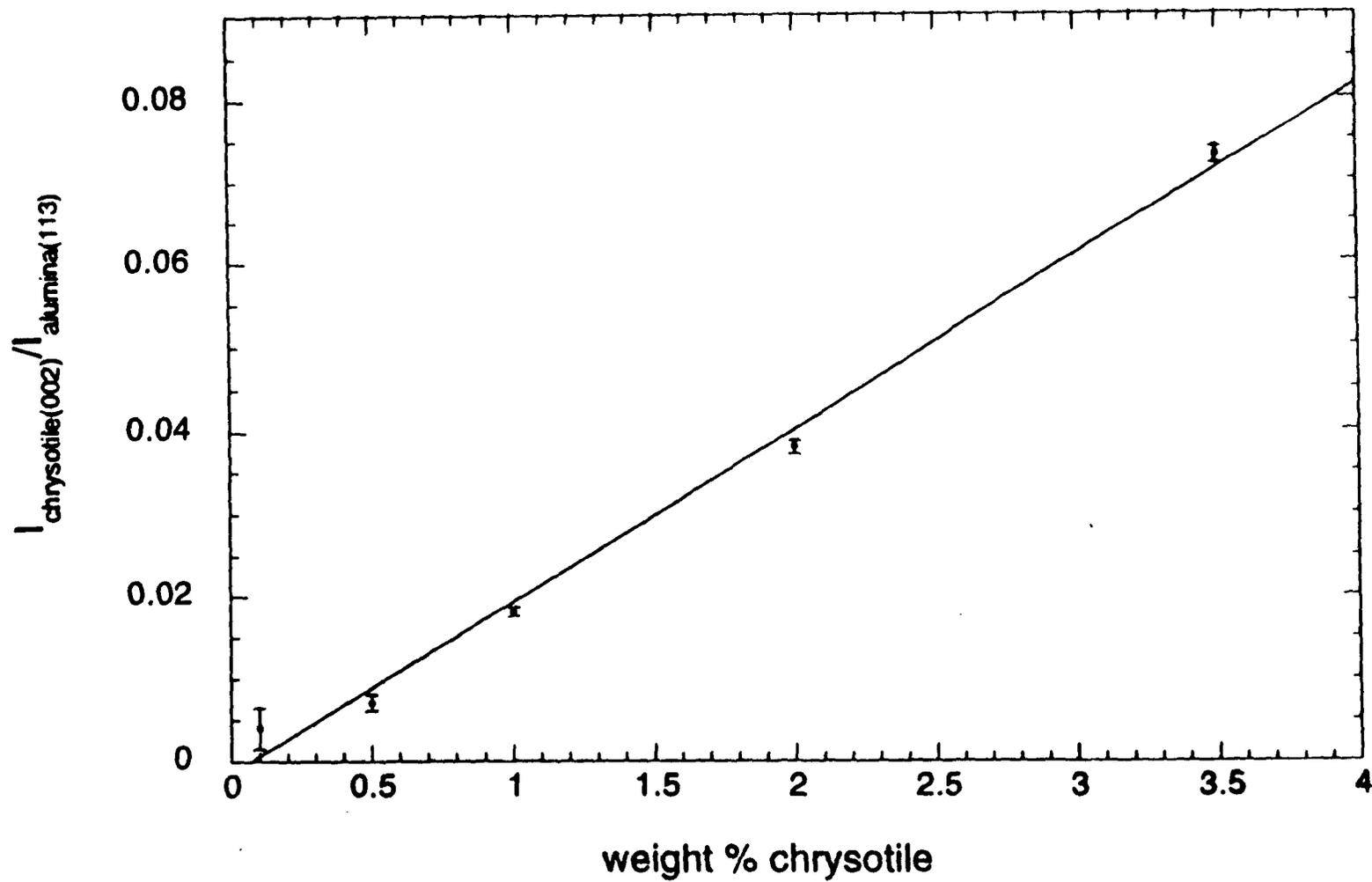


FIGURE 22

40



DMA (H₃ PO₄ + Fluorosilicate)

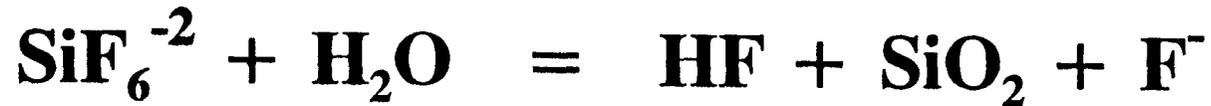
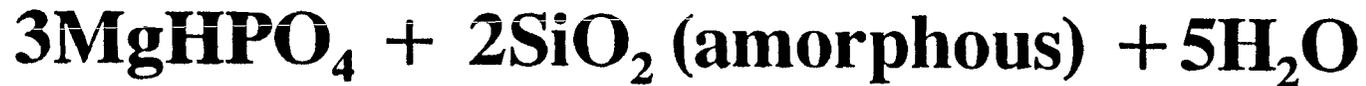


FIGURE 23

FIGURE 24

PRODUCT COMPOSITION FOLLOWING APPLICATION OF DIGESTION AGENT

Component	Approximate wt. %
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ $\text{Ca}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	55 - 65
$\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$	15 - 25
Vermiculite	10 - 20
CaF_2 , AlPO_4 , Fe_2O_3	<5
Amorphous SiO_2	2 - 5
Chrysotile	<1

The original product composition was approximately 63% Gypsum, 25% Vermiculite, and 12 % Chrysotile

Asbestos Digestion Project

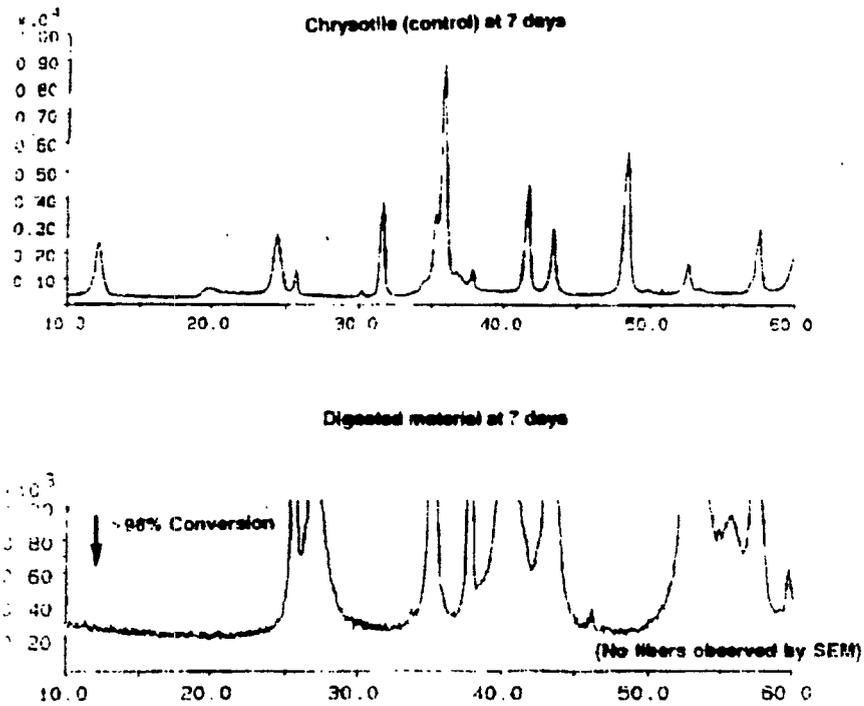
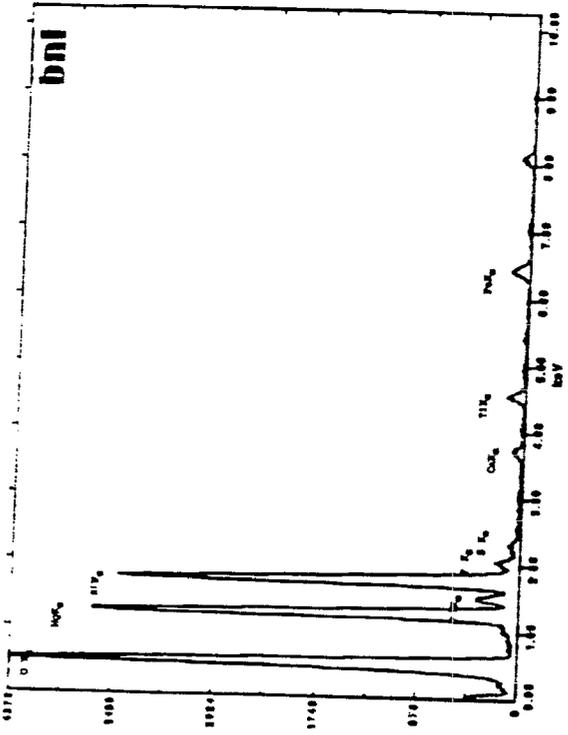


FIGURE 25



TEM micrograph of Chrysotile fibers.



EDS spectra of Chrysotile fibers.

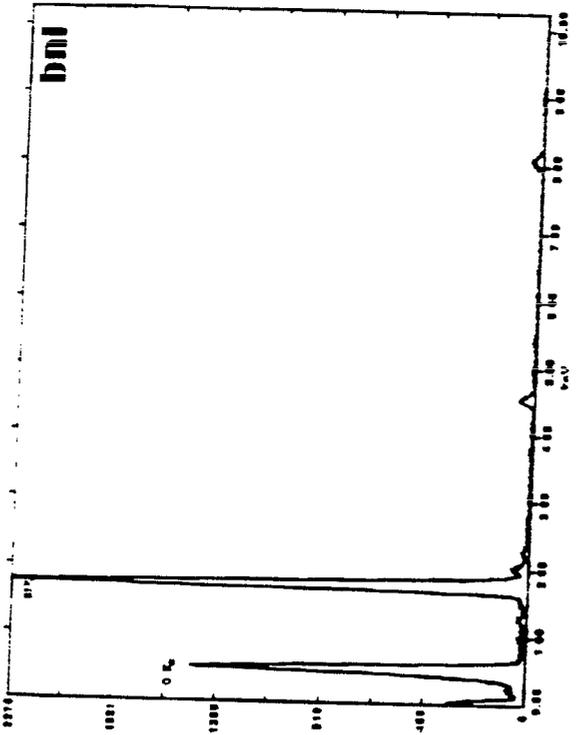


FIGURE 26

FIGURE 27

(Not shown.)

One of the ITF Facilities

XRD ANALYSES OF ITF SAMPLES

- **34 PANELS AND BEAMS**
- **9 CORES FROM EACH PANEL AND BEAM**
- **3 SECTIONS (DEPTH) FROM EACH CORE**
- **DUPLICATE ANALYSES -BNL, WRGRACE**
- **LABORATORY XRD, PLM, NSLS**

***ALL SAMPLES* FOR WHICH THE APPLICATION PROTOCOL WAS FOLLOWED SHOWED CHRYSOTILE AFTER TREATMENT TO BE < 1 WT % (VS. 12.7 % ORIGINALLY PRESENT)**

NOTE: REGULATORY AGENCIES CONSIDER ANYTHING BELOW 1% AS NON- ACM (ASBESTOS CONTAINING MATERIAL)

FIGURE 28

FIGURE 29

AIR QUALITY MEASUREMENTS

	TEST METHOD	OSHA PEL	ENGINEERING SCALE TESTS (ITE)	FIELD TEST
Asbestos fibers released during digestion process	NIOSH 7400 (PCM)	0.1 f/cc	0-0.0052	0-0.035
	Impinger (PCM)		0.002-0.0078	
	FAM (PCM)			
dry scraping of ACM wet scraping of ACM	TEM N10SH 7402	0.1f/cc	0	
	TEM N10SH 7402	0.1f/cc	0	
	N10SH 7400	0.1f/cc	0.0015-0.005	
	FAM	0.1f/cc	0.0002-0.0014	
Acid Droplets HF H3PO4	N10SH 7903	3 ppm	<0.01-1.42	0-1.2
	N10SH 7903	1 mg/m³	<0.01-1.09	
Acid Vapors HF	Diffusion Sensor	3 ppm	0.1-0.7	0-1.2
By-product Gases H₂ H₂S	Diffusion Sensor	LEL 4%	0-3% of LEL	
	Diffusion Sensor	10 ppm	0-0.7	

FIGURE 30

(Not shown.)

**The Bank Building on which
W.R. Grace did the Field Work**

FIGURE 31

BULK ANALYSIS BY XRD OF FIELD TESTS SAMPLES RESIDUAL CHRYSOTILE AFTER APPLICATION OF DMA

	RANGE Wt%	AVERAGE Wt%	TOTAL NUMBER OF SAMPLES TAKEN	NUMBER OF ≥1% CHRYSOTILE
Spray Test #8 (3/10 - 3/13)	0-0.22	0.02	28	0
Spray Test #9 (4/9 - 4/18)	0-1.46	0.13	57	1
Spray Test #10 (6/17 - 6/19)	0-4.23	0.14	57	2
Spray Test #11 (7/15-7/16)	0-0.81	0.13	40	0
Spray Test #12	0-0.7	0.02	50	0

Notes: (1) The initial wt% of Chrysotile was 15%

(2) These results are inline with cores from 34 beams and panels treated with DMA in the Engineering phase where the initial 12.7 wt% was reduced to <1 wt%.

Asbestos Digestion Project

XRD Analytical Method

Results from Virginia - Spray Test 11

Low = 0.00 Mean = 0.13
High = 0.81 Median = 0.05

Sample #	% Chrysotile	Sample #	% Chrysotile	Sample #	% Chrysotile
11-1	0.06	11-15	0.00	11-28	0.00
-2	0.03	-16	0.19	-29	0.00
-3	0.31	-17	0.12	-30	0.07
-4	0.00	-18	0.14	-31	0.05
-5	0.10	-19	0.04	-32	0.02
-6	0.81	-20	0.05	-33	0.00
-7	0.06	-21	0.16	-34	0.04
-8	0.00	-22	0.69	-35	0.09
-9	0.05	-23	0.66	-36	0.20
-10	0.00	-24	0.17	-37	0.00
-11	0.26	-25	0.19	-38	0.00
-12	0.04	-26	0.51	-39	0.00
-13	0.00	-27	0.10	-40	0.04
-14	0.04				

FIGURE 32

Asbestos Digestion Project

Virginia Spray Test Results

Airborne Fibers Monitoring

Spray Test #	PCM			TEM		
	NIOSH 7400 (Fibers/cc*)			NIOSH 7402 (Fibers/cc+)		
	High	Low	Mean	High	Low	Mean
10	0.0082	0.0004	0.0022	0	0	0
11	0.0159	0.0033	0.0076	0	0	0
12	0.0204	0.0016	0.0067	0.006	0	0.0008

* 8-hr TWA
† Area Samples

FIGURE 33

**COMPARISON OF TECHNOLOGY TO
BASELINE TECHNOLOGIES**

Work Breakdown	Conventional Abatement		Conversion Process	
	Percent of Cost	Estimated Cost	Percent of Cost	Estimated Cost
Negative Pressure Containment Setup	30	\$3.00	0	
Asbestos Containing Material Treatment	40	\$4.00	100	\$5.00
Negative Pressure Containment	20	\$2.00	0	
Cleanup/Teardown				
Disposal of Waste	10	\$1.00	0	

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FINDINGS:

- This asbestos conversion technology will save an average of \$5.00/square foot of abatement.
- The estimated cost savings to the U.S. government, State and local governments and U.S. industry for remediation over the next 25 years could be as great as \$50 billion dollars.

Source:

HAZWRAP, Lockheed Martin Energy Systems, Inc., 13 Dec 1995.

FIGURE 34

COSTS OF CURRENT REMOVAL VS. NEW IN-SITU METHOD

COST/FT² OF 3/4" THICK ACM

CURRENT METHOD

NEW IN-SITU METHOD

Site Preparation
Removal
Re-fireproofing

\$3.74
8.03
0.75

\$12.52

Site Preparation
Material + DMA Application
Neutralization

\$0.75
1.92
0.80

\$4.19

FIGURE 35

STATUS

- *Chrysotile (BNL, WRGRACE Patents)*
 - *BNL Large Scale Demos in DOE and Federal Facilities*
 - *WRGrace Commercialization in the Private Sector*

- *Amosite (BNL Patents)*
 - *US Navy, DOE, EPA, MarketSpan*

FIGURE 36

**ANOTHER LESSON LEARNED: CAREFULLY STRUCTURED
COLLABORATIONS DO WORK...**

- PEER-REVIEWED PAPERS AND PRESENTATIONS
- TRAINING OF POST-DOCS
- UTILIZATION OF LARGE FACILITIES
- PATENTS
- SAFETY AND REGULATORY AGENCIES EARLY INPUTS A BIG PLUS
- COMMERCIAL PROCESS
- POSITIVE PUBLICITY

FIGURE 37

DOE

NEWS

NEWS MEDIA CONTACT:
Kara Villami, 516/344-2345

FOR IMMEDIATE RELEASE
December 10, 1997

"Brookhaven Laboratory scientists have helped create an innovative, safe solution to a tough problem that affects people around the country. This is just one example of many achievements at Brookhaven, known for its contributions in medicine, basic research, energy and environmental science. Partnerships between Department of Energy laboratories and private industry consistently reap tangible rewards. In this case, we will make a difference in safely removing asbestos from schools, houses, offices and other buildings," said Secretary of Energy Federico Peña.

-DOE-

FIGURE 38

ACKNOWLEDGMENTS

Collaborators

Brookhaven National Laboratory

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L. Ciesluk
L. Dolhert
M. Hager
L. Hegedus
N. Krupkin
R. Milton
H. Mirano
D. Myers
R. Hu

FIGURE 39

ACKNOWLEDGMENTS-SUPPORT

The Asbestos Project was a success due also to the wonderful cooperation with, and support from others than the researchers involved, inter alia. The BNL Directorate, Department of Applied Science, The Light Source, Physics, Medical, ES&H, Technology Transfer, DOE Brookhaven Office and Headquarters, EPA and OSHA.

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- US EPA (**Tom Ripp**)

- US OSHA (**Dan Crane**)

FIGURE 40