

DECONTAMINATION OF UNCOATED CONCRETE FROM HAZARDOUS ORGANIC FLUIDS BY THERMIC TREATMENT

DEKONTAMINATION UNBESCHICHTETER BETONBAUTEILE MIT THERMISCHEN VERFAHREN

DECONTAMINATION DE BETON NON-REVETU PAR TRAITEMENT THERMIQUE

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SUMMARY

The non-biological decontamination of abandoned polluted areas with thermic methods is used successfully in situ, on-site and off-site. Experiences of cleaning concrete structures that are contaminated with hydrocarbons do not exist. Starting with a brief review of theories and models applied to drying technology a testing program and first results are presented.

Polarity, viscosity and surface tension of the testing liquids as well as the temperature dependent change of these parameters determine the effect of decontamination and the absolute rest contamination.

A further developed testing device is aimed at the optimal planning and implementation of thermic in-situ decontamination on concrete structures in practise. By a special measuring and control unit a total balance of decontamination is possible that enables the control of limits set by authorities or by the owner of the plant.

ZUSAMMENFASSUNG

Die nicht-biologische Dekontamination mit thermischen Verfahren wird bei der Altlastensanierung von Böden erfolgreich in-situ, on-site oder off-site eingesetzt. Erfahrungen bei der Reinigung von Betonbauteilen, die mit Kohlenwasserstoffen verseucht sind, liegen nicht vor.

Ausgehend von einem Abriß der Grundlagen und Modellierung hygrischer Transportprozesse aus der Trocknungstechnik wird über ein Versuchsprogramm

und ersten Ergebnissen berichtet. Polarität, Viskosität und Oberflächenspannung der Versuchsflüssigkeiten sowie die temperaturabhängige Änderung dieser Eigenschaften bestimmen Reinigungsleistung und Dekontaminationsgrad.

Ein weitergehendes Versuchskonzept hat das Ziel der optimalen Planung und Durchführung einer thermischen in-situ Dekontamination auf Oberflächen von Betonbauteilen. Eine meßtechnische Bilanzierung der Dekontamination ist gewährleistet und ermöglicht die Einhaltung von behördlichem Überwachungswert und Sanierungsziel des Anlagenbetreibers.

RÉSUMÉ

La décontamination non-biologique par procédés thermiques de terrains pollués abandonnés est utilisée avec succès in-situ, on-site et off-site. Il n'y a pas d'expériences avec le nettoyage d'éléments en béton contaminés avec des hydrocarbures. Partant d'un aperçu de théories et modèles appliquées à la technologie de séchage un programme d'essai et les premiers résultats réalisés sont présentés.

La polarité, la viscosité et la tension de surface des liquides d'essai ainsi que la modification de ces propriétés en relation avec la température déterminent l'efficacité du nettoyage et le degré de décontamination.

Un programme d'essai ultérieur poursuit le but de projeter et réaliser le mieux possible la décontamination in-situ de surfaces d'éléments en béton. Par mesurage et contrôle il est possible d'établir un bilan de la décontamination qui permet de respecter les limites de contrôles déterminées par les autorités ou le propriétaire des entreprises.

KEYWORDS: concrete, thermic decontamination, drying technology, heat transfer, rest contamination, in-situ monitoring and control

1. INTRODUCTION

There are numerous concrete structures in the chemical industry which have to provide the necessary safety against the pollution of soil and groundwater. To produce, decante and handle hazardous fluids the operator of a plant is obliged to make up a concept in case of damage or fault in the plant together with the application to obtain official approval [9]. The concept has to point out methods to guarantee successful decontamination in situ, on-site or off-site in a limited period of time. For the removal of such a damage there are no informations or experiences attained about useful methods, duration, limit of sanitation or monitoring. Temperature, amount and particle size of the polluted material and the physical/chemical characteristics of the hazardous fluids influence the basic process techniques according to previous experiences with the sanitation of abandoned polluted areas. Due to the microstructure of hardened cement paste, size and composition of the aggregates the available knowledge from soil cannot be transfered on concrete.

The cleaning rate per unit of time is crucial for developing a decontamination process for concrete. There is no non-destructive testing method to register in-situ a possible rest contamination after sanitation.

Thermic decontamination means a specific, controled drying-out of concrete from fluids penetrated by capillary absorption into the microstructure. The vapour pressure of the organic testing fluids are up to 10 times higher at 20°C than water, an important advantage for this sanitation method. Thus premises are set up for a conversion from liquid to gaseous state, overcoming linkage and frictional force and expelling the harmful fluids out of concrete. The results are interpreted on the basis of Krischer's studies [11] though this subject is very

different from hygral transport in porous media [2, 3, 6, 12, 13].

During thermic decontamination a concrete structure is subjected to thermal strains due to external heat if a state of eigenstress and imposed deformation develops. Limits are given in [9].

2. TRANSPORT PROCESSES

2.1 Capillary transport and diffusion

Thermic decontamination is a reversion of the specific states of sorption combined with capillary fluid transport [1, 7, 10]: mass transport starts with a saturated flow in the pores (capillary transport against gravity), unsaturated flow, vapour diffusion up to the state of desorption takes place afterwards. The monitoring is limited by a balance of adsorption and desorption established after a long period of time. Viscosity, surface tension and vapour pressure determine the course of saturated and unsaturated transport inside the interconnected pore volume. Polarity and dipole moment are decisive parameters for mono- and multimolecular layers on the walls of the pores and thus for the balance of sorption. Gas and vapour diffusion determine the drying course as shown in previous research [1, 3, 7, 11]. The transport can be described as a directed, one-sided diffusion process out of a capillary pore through a static air space.

2.2 Heat transfer

Radiation is energy transported by electromagnetic waves. This has to be taken into account for two substances of different temperature separated by air. The

basic equations of heat transfer from one to another parallel plate are given in [5, 8, 14, 15].

Thermal conduction means energy transfer within a material medium. Energy transmitting molecules are not stable in their home position, they vibrate (molecular heat conduction of solid specimens) or show an evenly distributed proper motion in all directions (n-type conduction in metals). The equations for heat flow are shown in [5, 8, 14, 15].

Both thermal radiation in pores and thermal conduction in solid components (hardened cement paste) occur in porous materials. If a liquid-vapour blend fills the pores of concrete there will be also heat transmission by convection.

2.3 Drying and decontamination course according to the two-capillary-modell of Krischer [11]

The evaporative drying of non-shrinking capillary systems will be demonstrated with two continuously combined capillaries of different radii. Both capillaries are filled with liquid. The liquid evaporates through the meniscus of the narrower capillary. This assumption is also admissible for concrete because there are more narrow capillaries than greater capillaries as results from investigations of pore-size distributions of concrete have shown and because of a higher capillary force p_k in narrow capillaries that sucks up fluid from the greater pores ($p_k \sim 1/r$). These mechanisms are superimposed to the effect of condensation of vapour in narrow capillaries according to the Kelvin-equation.

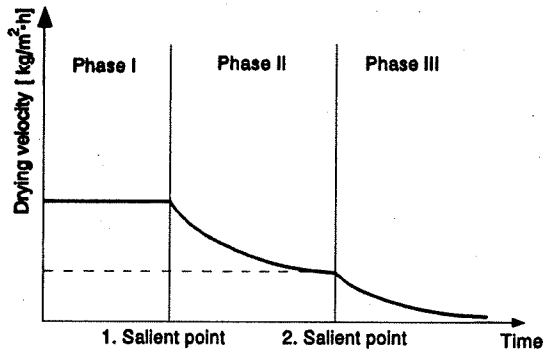


Fig. 1 Chronological course of drying velocity of a capillary porous material with hygroscopic properties [11]

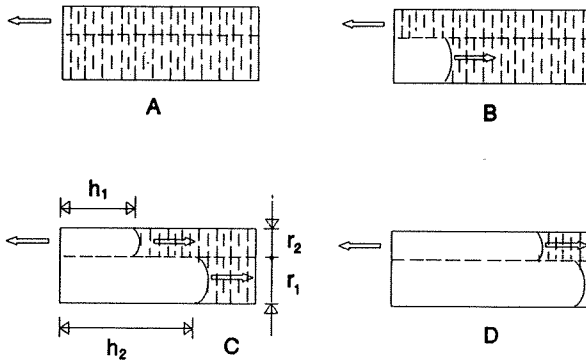


Fig. 2 Two capillary model according to Krischer [11]

Sections shown in Fig. 2 are based on following phase divisions:

Phase I, (A):

Start of the drying: liquid evaporates at the surface. The velocity of drying is constant.

Phase I, (B):

Drying through the meniscii of the more narrow capillaries the amount of evaporated liquid is sucked out of greater capillaries. The meniscus of the narrow capillary approximates to the form of a hemisphere. Mass transport is constant in phase I A and I B. It depends on surface temperature, difference of partial pressure between the surface of the solid body and the surrounding air and the mass transfer coefficients.

The mass flow m_{A1} becomes

$$\dot{m}_{A1} = \frac{\beta}{R_A T} (P_A'' - P_L)$$

/1/

β Mass transfer coefficient

$(P_A'' - P_L)$ Difference of partial pressure between saturated vapour pressure of gas A and air

R_A Specific gas constant of gas A

T Absolute temperature

Phase II, (C):

Capillary tensile force and inner friction have got the same number. The evaporating liquid cannot be sucked out of greater capillaries anymore. The meniscus of the narrow capillaries returns inside the solid body. The velocity

of drying decreases. A kink emerges in the velocity profile: 1. salient point (Fig.1). Krischner [11] and Manegold [7] identify this salient point as the balance of the capillary tensile force and the friction force according to Hagen-Poiseille's law. $\cos\Theta = 1$ is assumed by approximation (Fig.2):

$$2\sigma\left(\frac{1}{r_1} - \frac{1}{r_2}\right) = \frac{\dot{m}_A 8\eta h_2}{r_1^4 \pi \rho} \quad /2/$$

- η Dynamic viscosity
- σ Surface tension of the liquid
- ρ Density of the liquid

The mass flow occurring i.e. the diffusing substance per unit of time can be described as

$$\dot{m}_A = \frac{1}{R_A T} * \frac{1}{\frac{1}{\beta} + \frac{\mu h_1}{D}} * (P''_A - P_L) \quad /3/$$

- h_1 Depth of the liquid meniscus (depending on time)
- μ Diffusion resistance factor of the dry layer (h_1)

Equation /2/ is based on the assumptions that diffusion is superimposed to capillary flow and that the saturated vapour pressure is less than the absolute pressure.

Phase III, (D):

The wide capillary is empty. Only above the meniscus of the narrow capillaries a diffusion process takes place. Liquid absorbed at the border of the capillary is emitted (2. salient point, Fig. 1). Drying ends as the state of equilibrium is reached on the sorption isotherm depending on temperature, atmospheric moisture, interlinked porosity etc.

3. TESTING PROGRAM OF PRETESTS

Sufficient dimensions of the cylinders ($d=10$ mm, $H=10$ mm) guarantee an unimpeded fluid absorption during contamination (capillary suction test [DIN 52617]). Previous storage in the climatic chamber simulates the conditions of outdoor concrete in order to calculate the influence of the humidity in the pore system. Some specimens are dried to constant mass [DIN 18555]. The physically bound water is expelled. The capillary pores are now empty being able to take in testing liquids. Only the physical-chemical properties of the test liquids are decisive for the later decontamination process. Table 2 shows the physical-chemical properties of testing liquids used.

Water serves as a reference liquid because all attempts in drying technology [11] and in building physics [6, 12, 13] were carried out using water. The dynamic viscosity and the surface tension decrease with increasing temperature, as the steam pressure increases. The influence of temperature on physical properties of the test liquids is documented in [1].

The testing program with the liquids cyclohexane and butyldiglycole were reduced to a preparatory treatment (p.t.) at 105°C and a decontamination temperature of 60°C .

Table 1 Survey on testing program

Test Liquids	Concrete	Preparatory treatment (p.t.)	Temperature of decontamination
Acetone, Water Butyldiglycole n-Hexane, Cyclohexane, Diesel oil	R I L I (composition according [9])	climatic chamber: 20°C/65%r.F. and dried at 105°C	drying chamber (DC): 60°C and room conditions (RC): 20°C/40% r.h.

Table 2 Data of testing fluids [16, 17]

	Acetone		Water		Butyldiglycole		n-Hexane		Cyclohexane		Diesel Oil	
Chem. Formula	C ₃ H ₆ O		H ₂ O		C ₈ H ₁₈ O ₃		C ₆ H ₁₄		C ₆ H ₁₂		Mixture	
Boiling Point (°C)	56		100		230		68		104		Distillation range	
Water Solubility	infinite		infinite		infinite		no misibility		no misibility		no miscibility	
Density (kg/l)	0,79		1,0		0,954		0,66		0,94		0,86	
Temperature	20°C	60°C	20°C	60°C	20°C	60°C	20°C	60°C	20°C	60°C	20°C	60°C
Surface Tension (mNm ⁻¹)	23,70	~20	72,75	66,24	30,0	--	18,43	~15	25,2	~20	0,003	0,002
Dyn. Viscosity (mPas)	0,316	0,226	1,0	0,47	5,92	--	0,31	0,21	0,979	0,527	4	1,8
Vapour Pressure (bar)	0,233	~1,0	0,023	0,199	3E-4	9E-4	0,16	~0,6	0,104	~0,4	0,017	0,052

4. TESTING RESULTS

The degree of decontamination of the penetrated quantity of the liquid is given in [%]. This relatization compensates dispensions.

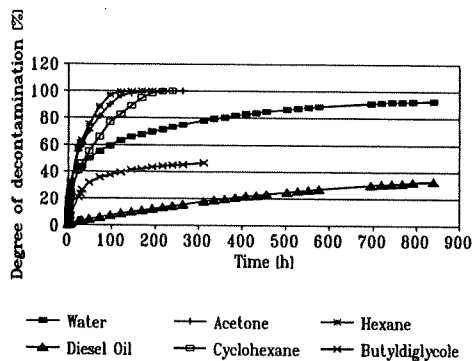


Fig. 3 Decontamination in the drying chamber (60°C), preparatory treatment 105°C

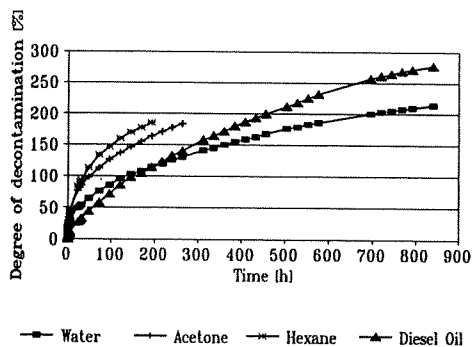


Fig. 4 Decontamination in the drying chamber (60°C), preparatory treatment 20°C

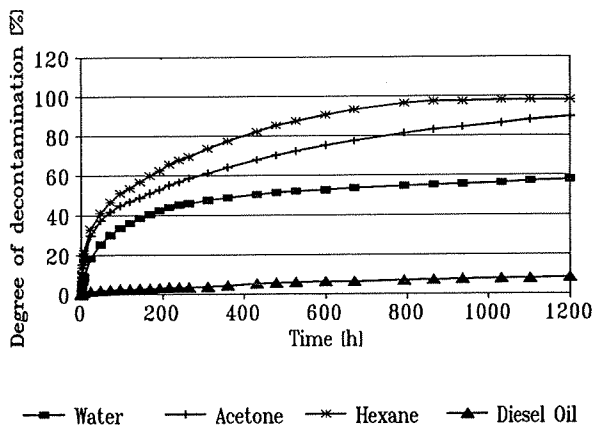


Fig. 5 Decontamination with room conditions, preparatory treatment 105°C

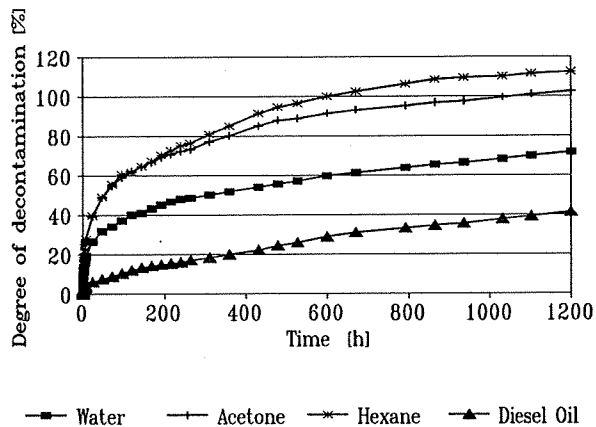


Fig. 6 Decontamination with room conditions, preparatory treatment 20°C

5. DISCUSSION

5.1 Preparatory treatment

By regression analysis with the dummy experiment the influence of different moisture is implemented. Results of 4 have to be corrected as follows:

**Decontamination course of the specimen = loss of testing liquid
± ad- or desorption of water**

A set up of functional equations is necessary for all boundary conditions, testing fluids and the dummy experiment. With this procedure a limit of decontamination at 100 % is possible by modelling. Grube and Spanka [18] used this simple method to determine the diffusion coefficient by weighing.

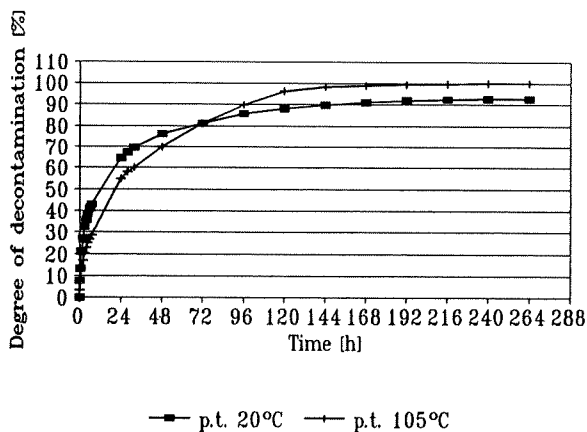


Fig. 7 Course of decontamination of acetone with the corrected numbers

In moist samples the amount of testing fluid which is to be decontaminated is less than in dry samples. This reflects the velocity of decontamination and is related to all liquids. The kind of preparatory treatment has no influence on the absolute time for cleaning (until reaching mass constance). This statement is verified by the results from determination of the remaining rest concentration. The influence of water miscibility of the test liquid on the course of decontamination cannot be quantified within this testing series. Comparing hexane und acetone (almost identical viscosity) the evaporated water reduces the absolute rate of decontamination in the same range.

5.2 Testing fluid

Dynamic viscosity, steam pressure and polarity of a liquid are responsible for cleaning. Acetone and Hexane having both a low viscosity and a high steam pressure reach after 1200 h (50 d) a degree of decontamination (RC) of almost 100 %. The remaining test liquid (rest contamination) is adhered to the pore walls. Acetone builds up sorbate layers due to its high polarity sticking better to the hardened cement paste. Thus acetone is less decontaminable than n-hexane (rest content max. 10 %, preparatory treatment 20°C). Thermic decontamination is unnecessary for acetone and hexane if the absolute time for decontamination is not considered. To collect and dispose the emissions (due to evaporation) with suitable measures is sufficient. Diesel oil shows the opposite of this effect: the cleaning capacity stayed lower than 30 % (degree of decontamination, DC 60°C). A time of experimentation of 900 h is not possible in reality therefore a degree of decontamination of less than 20 % is to be expected on the basis of a realistic estimation.

5.3 Gas-in-gas diffusion according to the "time-lag-method"

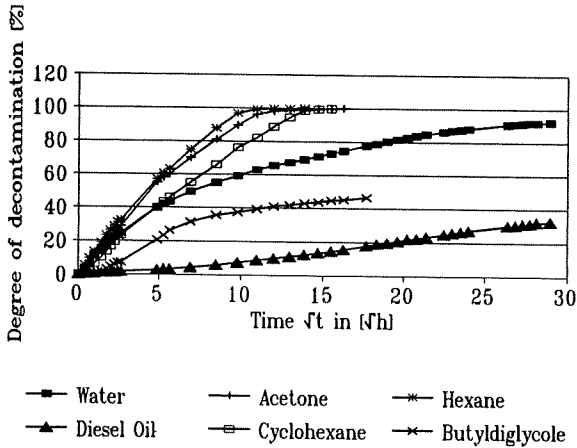


Fig. 8 Course of decontamination over the square root of time

Liquids with high steam pressure (acetone, hexane) have a linear course of decontamination up to reaching the equilibrium moisture content (degree of decontamination about 98 %). Thus an interpretation of the theory of Timofejew [4] and Crank [2] is possible. Timofejew and Crank expand the stationary diffusion current over a level of a liquid with an asymptotic approximate solution from unsteady diffusion current according to the Fick's 2nd law. After an acceleration period of time a linear course is noted.

5.4 Self-cleaning of acetone and hexane

Fig. 5 and 6 show an almost complete self-cleaning of acetone and hexane.

This confirms tests of Spanka [18] with methylene chloride having comparable properties: the time of contamination of the specimen was 3 days ($t = 1-3$ d). After one day ($t = 4$ d) about 90 % of the penetration volume is already released (ratio of 3rd day = 2200 g/m²; ratio of 4th day = 260 g/m²). The diffusion proceeding into the specimen is little (≤ 20 mg/m²).

The remaining content will spread however over the height of the specimen as long as a concentration gradient exists.

5.5 Temperature

The decrease of the dynamic viscosity reduces internal friction force; capillary conduct becomes better. Thus a capillary transport of liquid is guaranteed towards the meniscus for a longer period of time (Phase I, maximum velocity of decontamination). Therefore an increase of temperature generally improves the decontamination capacity.

An increase of temperature of 40 K leads up to a doubling of the degree of decontamination that is a bisection of the time of decontamination:

Diesel oil: 15 % to 35 % degree of decontamination (after 900 h)

Water: 65 % to 94 % degree of drying (after 900 h)

Hexane: 1200 h to 192 h time of decontamination

(degree of decontamination: 100 %)

Acetone: 1200 h to 240 h time of decontamination

(degree of decontamination: 100 %)

5.6 Content remaining

Four specimens with following preparatory treatments have been analysed:

Acetone (drying chamber)		Hexane (drying chamber)	
p.t. 105°C	p.t. 20°C	p.t. 105°C	p.t. 20°C

Parts of specimens out of a depth of about 40 mm had been crushed ($4 \text{ mm} \leq d \leq 8 \text{ mm}$, aggregates and parts of hardened cement paste) for gaschromatic analysis.

Table 3 Remaining concentration of organic solvents

Test Liquid	Acetone		n-Hexane	
	105°C	20°C	105°C	20°C
Preparatory Treatment				
Concentration Remaining	28,7 mg/kg	41,8 mg/kg	0,92 mg/kg	0,94 mg/kg

- A remaining concentration up to maximum 42 mg/kg of a specimen with about 3,5 kg leads to an absolute residue set of 0,142 g.
- The homopolar liquid hexane does not show (0,92 mg/kg \approx 0 g/kg) any further rest contamination. Acetone forms layers of sorbates.
- The remaining content of different treated specimens is neglectibly small. Usual preparatory treatment of a specimen will be of minor importance if the testing liquid's vapour pressure is higher and viscosity is lower than water. A complete (100 %) decontamination is reached in the same time.

6. TRANSFER TO PRACTICE

Previous results have shown that thermic decontamination is a suitable and successful method for the sanitation of concrete contaminated with organic fluids. For practical application "in situ" (meaning on the spot) there is need for checking and classification of the contamination potential by a gaschromatographic analysis and for a monitoring and controlling unit (MCU) to document the progression and the end of decontamination (see Fig. 9): a heating spiral supports gas evolution by increasing the vapour pressure gradient. An individually variable temperature is fixed at the concrete surface during decontamination. Over the height of the sample the temperature gradient is measured at different positions. In order to fix a directed concentration gradient towards the upper surface of the specimen the contaminated gas is thinned and transported by N_2 as flush gas. The system is closed, a balance of decontamination is possible by analyzing the concentration in the delivering gas by a gas detector (PID). In case of high penetration depths caused by the contamination the diffusion front can reach the soil [9]. Radiation expedites this transport. This is checked by the construction of a container filled with activated carbon being analyzed for the penetrated fluid at the end of the test. Test results from testing fluids of Tab. 2 are currently evaluated, a subsequent publication devoted to this subject will follow.

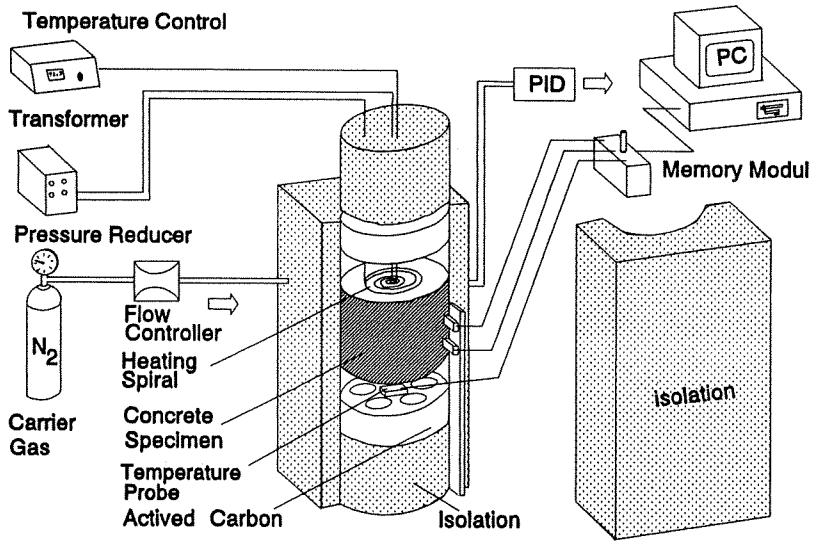


Fig. 9 Testing device for simulation of in-situ decontamination

7. ACKNOWLEDGEMENT

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