

Radiolysis in intermediate level waste of the STAR process

F. Minot

CEA Saclay, CAD/DEN/DEC/SLS/LPS, Centre CEA de Cadarache, 13108 St Paul lez Durance, France

Abstract

The STAR facility (**S**tation de **T**raitement, d'**A**ssainissement et de **R**econditionnement) is a high-activity laboratory, extension of the Laboratoire d'Examen du Combustible Actifs, making up the French Basic Nuclear facility INB55. STAR treats part of the fuel coming from the UNGG system (Natural Uranium Graphite Gas system used in France from 1955 to 1994) used by the CEA between 1960 and 1980 for R&D purposes. These fuels are mainly stored under water in the Cadarache center facilities (INBs 22 and 56) and those of Saclay (INB 72). They are packaged in steel containers, 40% of which are estimated to be degraded fuels, due to the reaction of the fuel elements with the water which might have been in contact with it. STAR was thus built and started up in 1994 in order to clean up the 2600 UNGG and D₂O fuel elements of the CEA.

The laboratory is also used as a logistic support to the experimental units using two of the three hot cells for examinations, cutting and gas sampling on PWR fuel rods. This activity represents about 10% of the total laboratory activity.

The aims of the processes used by STAR are :

- to thermally stabilize the fuel which has reacted with storage pool water
- to recondition the stabilized fuel to allow for an average term storage guaranteeing its confinement.

The fuel elements in steel containers are brought to STAR packaged in rubber enclosures (to prevent contaminated water from leaking) using horizontal transport casks. These are placed against the entry hatch of the treatment cell, and their contents are transferred in the cell under inert gas atmosphere.

The containers are opened, their water removed and contents inventoried. The toxic elements are removed (epoxide resin, magnesium clads...) and treated as specific wastes. The treatment of the fuel elements is carried out according to three thermo-chemical operations, in a specific oven :

- drying at 100°C under argon flow,
- de-hydridation at 430°C under argon flow to decompose uranium hydrides,
- progressive oxidation at 250°C so as to oxidize the metal uranium by sweeps and successive pressurizations with an argon current with an oxygen content increasing up to 20 vol %.

The products thus stabilized are placed in seal-welded canisters. These canisters are transferred to the second cell where they are weighed and decontaminated prior to being transferred in the third cell to be temporarily placed in baskets in the storage pits of this cell. They are then conditioned in stainless steel containers under inert atmosphere and sent to the CASCAD facility.

The wastes

Besides the usual wastes from nuclear facilities (gloves, protective shoe cover...) of very low activity, all of the STAR operations generate specific wastes considered as sub-products from the treatment process and essentially coming from the treatment cell. The separation is then made between : the araldited wastes conditioned in stainless steel canisters and stored in the pits of Cell 3, pending a decision on their removal ; the magnesiate wastes, conditioned under inert gas in specific cans and sent to INB56 for storage ; and finally the technological wastes.

These technological wastes consist of initial fuel containers and container bases and rubber enclosures, booting and remote manipulator parts, vinyl, failed canisters and all the usual

working material needed in a hot cell (tools, tubes, steel sheeting, glass, cotton, and fabric). The wastes are highly contaminated and are thus irradiating. All of these wastes are divided into four main categories :

- Steel wastes
- Non-steel wastes (aluminum, lead)
- Plastics
- Cellulose wastes

The last two categories are of hydrogenated materials, thus subject to radiolysis. The residual contaminated water from the containers is collected and mixed with cement to form specific wastes, regularly characterized.

The containers used are steel drums of 50 liters in volume (H=0.62m, D=0.38m) closed with a lid kept in place with three staples. A foam joint under the lid ensures general tightness. These are then protected by vinyl and placed in the treatment cell, filled and removed without their protection into a upper shielded hatch.

The containers are weighed, closed, their dose rates measured, decontaminated and placed in their transport cask, which have beforehand been placed in the shielded hatch. The package is then removed, decontaminated and sealed tight.

The containers are thoroughly characterized : their contents are identified (materials, volumes and masses) as are their nuclear properties ; the nuclide masses and the activities are calculated using the total mass of the container, the dose rates measured upon contact and at 50 cm, and the isotopic spectrum of the STAR facility.

The cask used, an RD30 in a RD31 protection (more simply RD30/31) allows 14 containers to be transported to the treatment station, respecting European regulations. Initially, a waste package is thus made of a tight cask whose internal cavity can accommodate 14 containers and roughly 1000l of air at atmospheric pressure.

The contents of the containers is irradiating, a part is subject to radiolysis , which means we might have a release of hydrogen with accumulation of gas in the containers or in the internal cavity of the package. The transport of the package and its later opening are then dangerous because of the potential increase of its internal pressure and of the inflammation risk if its H₂ content is close to 4% vol.

Diffusion of H₂ in containers

By using dynamic flow measurements and diffusion measurements with helium spectrometry, it is shown that hydrogen cannot accumulate in the containers and completely diffuse towards the internal cavity of the package.

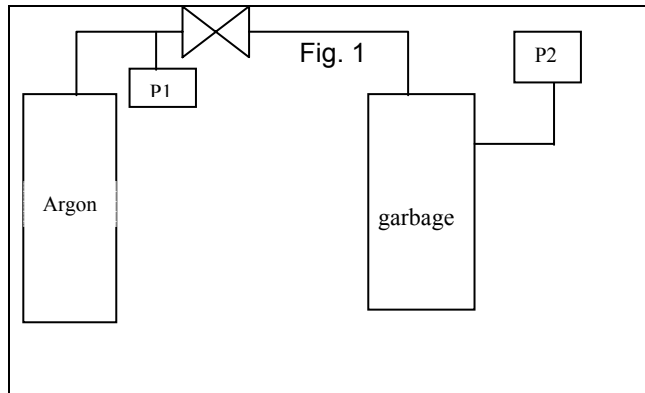
III-1 Dynamic flows

By using the device fig. 1, the evolution of P2 pressure in the container is measured versus the P1 driving pressure (Table 1).

Table 1:

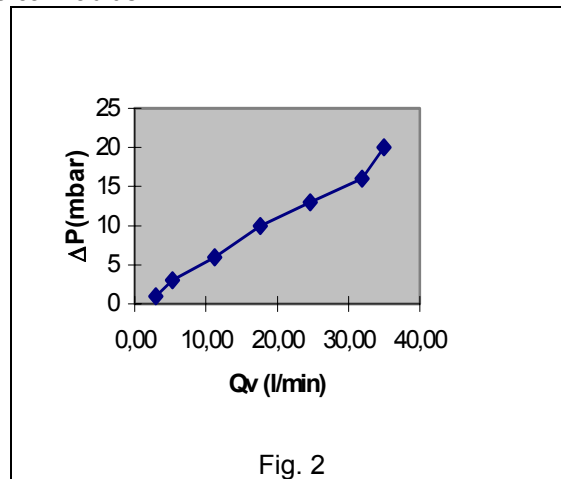
P1 bar Abs	P2 mbar Abs
1,1	986

2	1 000,6
3	1 010,1
4	1 019,9



These measurements show that the containers have such a leak rate that it is impossible to increase the internal pressure in any significant way. For an initial pressure of 1.1 abs bar, an expansion time of 2 seconds is measured (9 seconds with an overload of 75 kg). With the same device, at low driving pressure, the leak rate of the container was measured (Fig. 2) versus the overpressure compared to atmospheric pressure. An overload of 40 kg placed on the container simulated a second container stacked on the first as is the case in the RD30/31 package. The pressure drop is a linear function of the volume flow rate ; it can be modeled using Poiseuille's law in laminar regime :

$\Delta P = \frac{8\eta Q_v l'}{2\pi r l^3}$ where l and l' are typical sizes of the flow trough the joint; η the viscosity, Q_v the flow mass; r the garbage can radius.



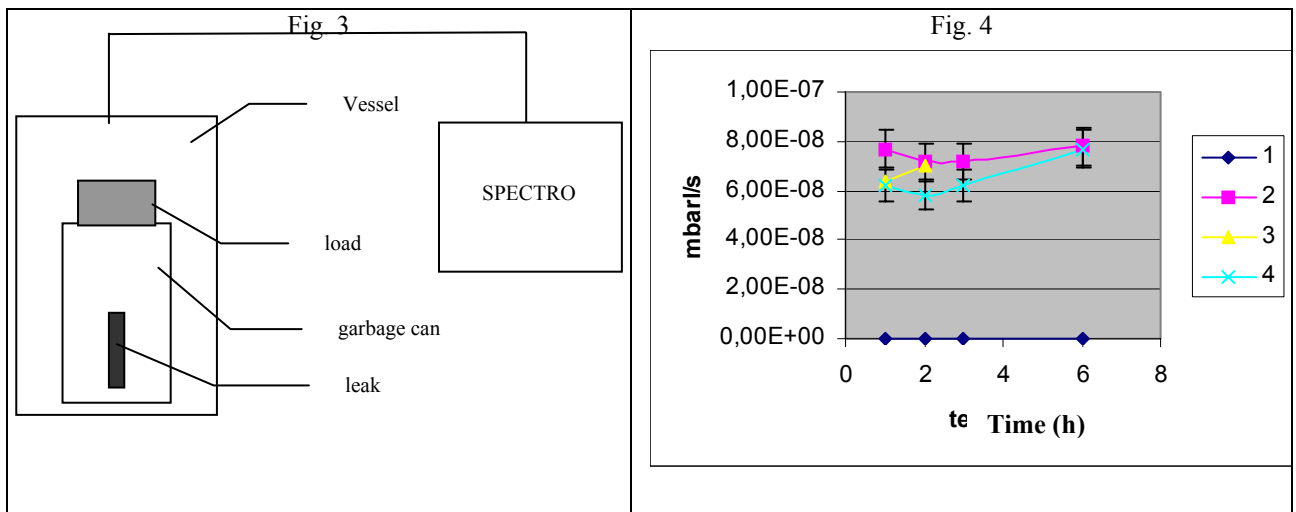
Let us suppose that the hydrogen produced by radiolysis increases the internal pressure of the container, initially under atmospheric pressure, of 0.1%. The overpressure is then of about 1 mbar. In view of the previous measurements, there is a flow from the container to the internal cavity of the package of 3l/min at 0.1% of H₂, thus an apparent production of 3ppmV/min (ppmV : part per million in volume) or 4300 ppmV/d of H₂ in the internal cavity. This is incoherent with the several dozen ppmV/d of production of H₂ measured in the cavity as will be seen later. It is thus

not possible to consider having a significant production of hydrogen in the containers with retention (since a low pressure is enough to establish a flow). Thus, it can be said that H₂ leaks out as it is produced at infinitely lower rates. We are therefore in the presence of a gaseous diffusion.

III-2 Helium spectrometry measurement

Using the device Fig. 3, the leak rate in helium in the following configurations was measured :

- 1-Container alone in the vessel
- 2-Standard leak in the vessel
- 3-Standard leak in the container in the vessel
- 4-Same with a load of 40 kg



The results are presented in Fig. 4 .

The leak rate measured by spectrometry when the leak is in the vessel is very rapidly identical to that measured with the leak in the overloaded container. Helium is detected independently from the presence of the container ; the gas thus diffuses perfectly through the foam joint.

Helium and hydrogen have similar properties in terms of diffusion. A leak of $8 \cdot 10^{-9} \text{ Pam}^3/\text{s}$ on a container means a global leak rate of $1,2 \cdot 10^{-7} \text{ Pam}^3/\text{s}$ for a loaded package. With a free volume of 1000 l, the increase in pressure of the package initially at atmospheric pressure is of $1,2 \cdot 10^{-7} \text{ Pa/s}$, in other terms 0,1 ppmV/d. This simulation is about 1000 times less than the productions measured on the packages. The diffusion of hydrogen from the container towards the internal cavity of the package is thus complete.

All of these measurements therefore prove that there cannot be any accumulation of hydrogen in the containers and that the hydrogen produced rapidly diffuses towards the internal cavity of the cask.

Quantization of radiolysis

The production of H₂ in the internal cavity of the package was quantified and modeled by radiolysis on 6 packages.

IV-1 Sampling, analyses

The presence of the container does not affect in any way the diffusion of H₂ in the package. The samplings are thus made in the upper part of the cask under the lid. A device developed by the CEA allows the circulation of the internal atmosphere of the package in a tight loop, all the while measuring the gas flow rate, pressure and temperature. This device also allows the sampling of gas in 500 ml pots. A circulation under the tight lid of the RD30/31 is thus created, the upstream of the circulator being in the center of the lid, the downstream in the periphery to homogenize the free internal volume. The circulation time chosen is the time necessary to mix a volume equal to the free volume of the package. The sample is then taken by filling the pot, which has beforehand been conditioned under vacuum, after stabilizing temperatures and pressure. The quantity of gas sampled is determined by measuring P and T before and after the sampling.

The samples are analyzed by Gas Chromatography. The device is calibrated for concentrations from 50 to 5000 ppmV. The detection limit is 10 ppmV, the values measured lower than 50 ppmV being only indicative. Each measurement point is sampled twice, and those samples for which the mixing time was insufficient were rejected.

IV-2 Results, interpretation

The quantity of hydrogen produced (Fig. 5,6) is a function which we assume to be linear versus time, with a significant uncertainty due to :

The chromatography, particularly at low contents.

The estimation of the quality of homogenization : the samples whose mixed volume is lower than the free volume of the package are rejected.

The knowledge of the free volume of the package :

The pressure measurements at 0.5 mbar near the package before and after sampling enable the free volume for each package to be determined. All of the samples thus help to establish that the average free volume of a package is of 1000 l ± 18%.

The knowledge and correction of the volume lost by the package at each sampling. The analysis of the results shows that these lost volumes are not very significant ; however, this induces an error of 4% on package D.

These last two difficulties disappear if only volume proportions are used, in other terms ppmV/d. The volume of hydrogen produced (in ml/d) is then a first approximation for a free volume of 1000l given by :

$$1 \text{ ml/d} = 1 \text{ ppmV/d}$$

The productions in ppmV/d are then graphically determined :

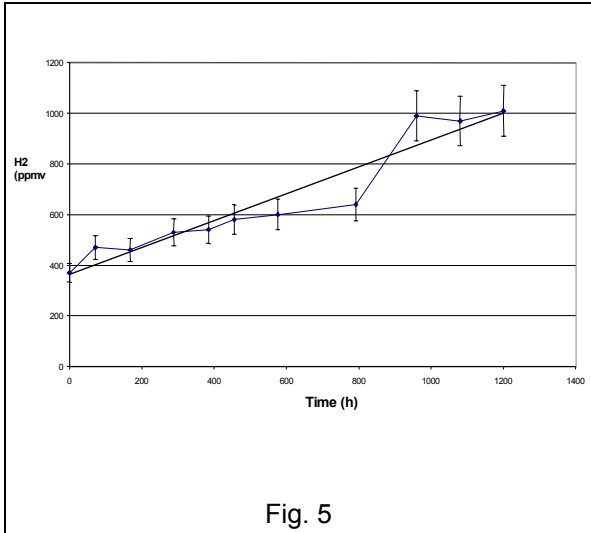


Fig. 5

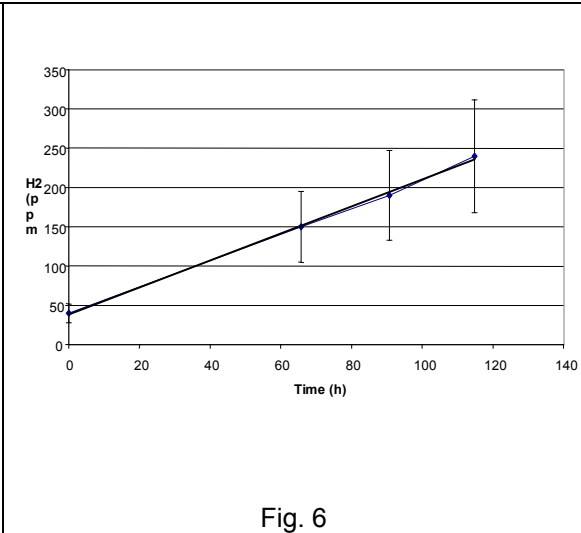


Fig. 6

By taking into account the gas chromatography measurement uncertainties, the following productions are obtained :

Package	Minimum ppmV/d production	Maximum ppmV/d production	Average ppmV/d production selected
B	7.1	15.8	11.5 +/- 30%
C	26	56	41 +/- 30%
D	8.1	15.5	11.8 +/- 30%
E	18.3	24.6	21.4 +/- 10%
F	28.6	38.6	33.6 +/- 10%
G	10	13	11.5 +/- 10%

The maximum production is obtained by the measurement point which gives the line with the greatest slope, the maximum measurement uncertainty being included.

The minimum production is obtained by the measurement point which gives the line with the least slope, the minimum uncertainty being included.

Moreover, the quantity of H₂ leaking from the packages when the latter are opened has been estimated. The H₂ produced is only partly released, the residual quantity being a maximum of 36% of the quantity produced during the same period with a tight package.

Finding a simple correlation

A rough estimate of the masses of radiolysable and non-radiolysable materials as well as all the nuclear characteristics has been made : mass of Pu; α, β, γ activities for each package, and for each the following are calculated :

$$\frac{H_2(\text{ppmv/d})}{\text{masses}}$$

$$\frac{H_2(\text{ppmv/d})}{\text{Pu}}$$

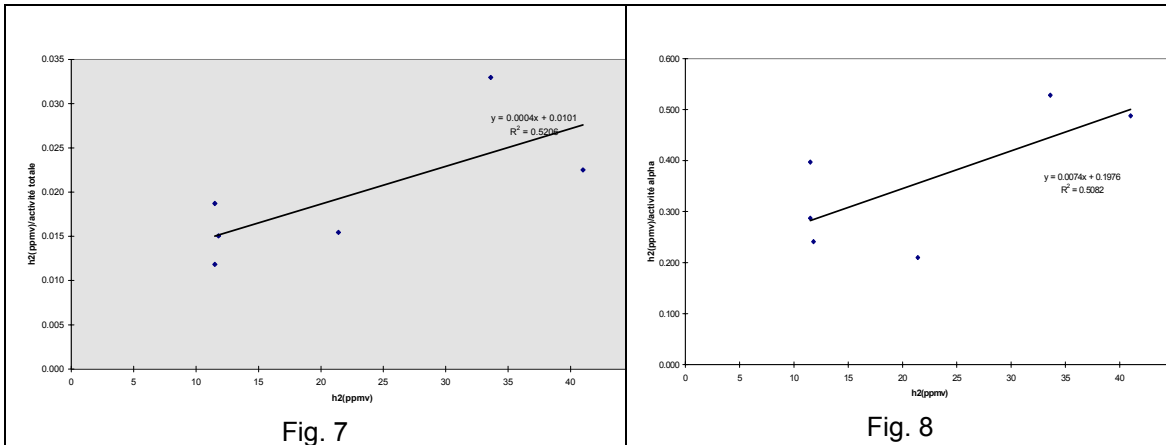
$$\frac{H_2(\text{ppmv/d})}{\text{Activities}}$$

Which gives:

	H2 ppm/d	$\frac{H_2(\text{ppmv/d})}{\text{radiol. mass}}$	$\frac{H_2(\text{ppmv/d})}{\text{non radiol. mass}}$	$\frac{H_2(\text{ppmv/d})}{\text{total mass}}$	$\frac{H_2(\text{ppmv/d})}{\text{Pu total}}$	$\frac{H_2(\text{ppmv/d})}{\text{Pu9}}$	$\frac{H_2(\text{ppmv/d})}{\text{total activity}}$	$\frac{H_2(\text{ppmv/d})}{\text{a activity}}$	$\frac{H_2(\text{ppmv/d})}{\text{bg activity}}$
B	11.5	0.491	0.037	0.035	4.435	5.838	0.012	0.397	0.012
C	41	2.124	0.108	0.103	4.130	5.341	0.022	0.488	0.024
D	11.8	1.035	0.027	0.026	2.041	2.640	0.015	0.241	0.016
E	21.4	0.977	0.059	0.055	2.159	2.792	0.015	0.210	0.017
F	33.6	1.273	0.102	0.095	4.473	5.786	0.033	0.528	0.035
G	11.5	0.341	0.032	0.030	2.429	3.142	0.019	0.287	0.020

A perfect linear correlation would be that which would give a constant value to one of the ratios. Or even that of the function : $\text{ratio} = f(H_2)$ is a line of nil slope and whose linear regression coefficient is equal to 1.

In practice, the correlation to select will be: $\text{ratio} = f(H_2)$ whose fit line has the smallest slope and highest linear regression coefficient. After study, we obtain (Fig. 7, 8):



The correlation to be used is thus that function of the **total activity**.

The production of hydrogen can then be estimated linearly versus the total activity of the package ; the proportionality coefficient being the average value of the ratio $\frac{H_2(\text{ppmv/d})}{\text{total activity}}$:

$$H_2(\text{ppmv/d}) = 0.02 \times \text{total activity} \pm 65\%$$

The F package is specific as it contains a filter loaded with PWR fuel which is not taken into account by the STAR isotopic spectrum for the calculation of activities. The same reasoning excluding it, gives :

$$H_2(\text{ppmV/d}) = 0.017(\text{ppmV/dGBq}) \times \text{total activity(GBq)} \pm 35\%$$

Verification

For the packages estimations of production are calculated with the expression :

$$H_2(\text{ppmV/d}) = 0.02 \times \text{total activity} \pm 65\%$$

	Time estimated since closure (h)	H2 produced calculated (ppmV)	H2 produced measured(ppmV)
B	72	58±37	33±17
C	138	209±136	240±72
D	1200	783±508	640±60
E	168	193±125	150±22
G	168	85±55	110±11

The estimated values are thus within the margin of error of the relation found.

Determination of radiolysis efficiency

The G factor is the number of H₂ molecules produced by 100 eV of absorbed ionizing energy.

This energy is seen in a residual power in the wastes, and for those coming from STAR:

$$p = 100\text{mW/kg(U+Pu)}.$$

The number of moles N formed by **hour** by radiolysis is given by :

$$N = \frac{GP}{2676} ; P \text{ residual thermal power (W), 2676 unit conversion factor.}$$

Thus the volume at 298K, 1 01.3 kPa in liters of H₂ produced daily is:

$$V=24 \times 22,4N$$

And production rate for a free volume of 1000 l :

$$H_2 (\text{ppmV/d}) = 10^3 V$$

By taking G=0.39 (coherent with the values given by the references 1 to 3), we obtain:

	H2 ppm/d measured	H2 ppm/d Calc 0,02activity	M U+Pu (g)	P(W)	H2 ppm/d Calc G=0,39
B	11,5±3,5	19,4±12	1066,6	0,11	8,36
C	41±12,3	36,4±23	3253,9	0,33	25,49
D	11,8±3,6	15,7±10	1896	0,19	14,86
E	21,4±2,1	27,6±17	3119,9	0,31	24,44
G	11,5±1,1	12,2±7	1488,4	0,15	11,66

The productions calculated with an efficiency of G=0.39 are in agreement with the H₂ production measurements and with the model previously established.

The radiolytic efficiency of STAR wastes is thus of 0.39

Conclusion

The study of the production of hydrogen in transport packages therefore raises several difficulties :

- Knowledge on the contents of the waste
- Knowledge on the dates of tight closures
- Difficulty of sampling
- Accuracy of gas chromatography measurements at low values.....

A simple correlation is not easy to obtain. However, one can use the following average correlation :

$$H_2(\text{ppmV/d}) = 0.02 \times \text{total activity} \pm 65\%$$

$$G=0.39$$

It is to be reminded that this correlation is only valid for those technological wastes coming from STAR cells.

The application of the above formula to three loading examples, gives the times required to reach the fourth of the inflammability threshold, 4% of H₂. The explosion threshold is of 18%.

Total activity (GBq)	Time needed to obtain 1% of H ₂ (d)	Maxi time needed to obtain 1% of H ₂ (d)	Mini time needed to obtain 1% of H ₂ (d)
1300	385	1100	232
2600*	192	550	116
6500*	77	217	47

* : extrapolated values

These values must be understood as starting at the time when the cask is loaded.

In conclusion, for the transport and opening of the packages, we recommend:

- For a total package activity of less than 2 600 GBq, to unload the RD30/31 within 116 days.
- For a total package activity of 2 600 GBq to 6 500 GBq, to unload the RD30/31 within 47 days.

If the package is not unloaded within these times, it must then be opened and reconditioned by air circulation (free volume renewed ten times), thus allowing to reach a nearly nil H₂ content. The package will then have returned to initial loading conditions.

References

- [1]: Hill, Radiation Chemical yields: G values, in Polymer Handbook
- [2]: Arakawa K and al, Radiation induced oxidation of polyethylene, ethylene-butene copolymer, and ethylene- propylene copolymer. Journal of polymer science, 1982. 20 pp 2681-2692
- [3]: Reed DT and al, Radiolytic gas production in the alpha particle degradation of plastics. Waste management 1992.