

SNO-STR-92-012

Some Preliminary Considerations about Cover Gas

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Scope

The scope of this document is to discuss some preliminary considerations for the selection of the cover gas system for Sudbury Neutrino Observatory .

Objectives

The main purpose of the Cover Gas System is to reduce the amount of O_2 in the water system (H_2O and D_2O) so as to inhibit the development of aerobic microorganisms. As a preliminary target we will aim to reduce the amount of O_2 dissolved in the water by a factor of 1000 or better from the normally present in deionized water.

General considerations on aerobic cells

In potable water, the amount of O_2 is about $10 \mu g(O_2)/g(H_2O)$. Under this condition, the number of cells per ml (N_{cells}) can be as large as 10^8 cells/ml. In this condition, there is a visible turbidity. According to our colleges form biology:

$$N_{cells} \propto [O_2] = \text{Concentration of } O_2 .$$

If we reduce the amount of O_2 by a factor of 1000, then at least the aerobics cells in water will decrease at a level bellow 10^{-6} , which would assure an optically clear water, provided that the nutrients of anaerobic cells is also controlled.

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Requirements and Constraint:

- Not to introduce sources of radioactivities in either the H_2O or D_2O .
- Not to enhance the corrosive properties of the water (H_2O and D_2O).
- Be reliable in term of personal safety.
- Cause the least impact on the budget of SNO.
- Require minimum maintenance.
- If possible provide a mechanism to reduce the radioactivity in the vessel, originating from Rn emanations.

Some Notation:

To set the scale of the problem and to introduce a common vocabulary we will introduce the following definitions:

V_i	= Total volume of the Cavity	$\sim 7000 \text{ m}^3$
V_f	= Remaining volume of cavity after water filling	$\sim 50 \text{ m}^3$
$V(t)$	= cavity atmosphere volume = $V_i - \text{Vol}(H_2O) - \text{Vol}(D_2O)$	
T_{fil}	= Filling time (~ 5 month)	~ 150 days
t	= Time in days	
$p_i(t)$	= Fraction in volume of i component in the cavity atmosphere as a function of time.	
$p_i^0(t)$	= Initial fraction in volume (same a molecular fraction) of component i .	
P	= Pressure of cavity atmosphere [mb]	
$H(t)$	= Input flux rate of cover gas in [m^3/h]	
$Q(t)$	= $P * H(t) = \frac{dn}{dt} R T$ \sim influx of molecules per unit of time	
$q(t)$	= Enrichment (%) of the cover gas in the inlet flux.	
T_{wait}	= Time of cover gas recirculation before water filling begins.	

General considerations and assumptions:

We will assume throughout this discussion that the pressure (P) and the temperature (T) of the cavity atmosphere remains constant (or vary adiabatically) throughout the whole process. Similarly we assume that the volume of the cavity atmosphere varies adiabatically, i.e the process of filling is sufficiently slow so that the volume of of the cavity atmosphere can be assume to be constant at each instant. We will consider that the cavity atmosphere is in thermodynamic equilibrium, i.e. the gas is completely mixed at a constant $p_i(t)$, T and P . We will consider that the outlet flux has this equilibrium composition ($p_i(t)$). Since P , T and V are "constant", the influx [m^3/h]

of gas is equal to the outflux [m³/h].

Toy Model: In order to have an intuitive picture of the problem under consideration, let's solve the following problem: consider a constant volume V being pumped in at a given rate H [m³/h] of pure cover gas, i . Let's calculate the time evolution of the volume fraction $p_i(t)$.

$N_i(t)$ = Number of molecules of type i in V at time t .

$$dN_i(t) = k(1 - p_i(t))H dt \quad (1)$$

$N_T = kV$ = Total number of molecules in V .

here k is the constant of proportionality between N and V .

$$\frac{d p_i(t)}{dt} = \frac{d N_i(t)}{N_T dt} = (1 - p_i(t))H/V$$

$$\frac{d p_i(t)}{dt} + \frac{H}{V} p_i(t) = \frac{H}{V}$$

$$p_i(t) = (p_i^0 - 1) \exp(-t/\tau) + 1$$

$\tau = \frac{V}{H}$ = cycling time.

If the the influx of cover gas were not 100% pure in the specie i , but had a purity of q_i^0 , then the expression of $p_i(t)$ would be:

$$p_i(t) = (p_i^0 - q_i^0) \exp(-t/\tau) + q_i^0$$

Improved Model: if we allow V , H and q_i^0 to vary adiabatically, the last equations become:

$$d p_i(t) = (q_i^0 - p_i(t)) \frac{H(t)}{V(t)} dt$$

and

$$p_i(t) = p_i(t - dt) + d p_i(t)$$

In this last case the equations have to be solved numerically. The figures 1 to 9 describe the variation of $p_i(t)$ for different scenarios.

Description of different scenarios:

1. **Piping gas from the surface:** This alternative require a piping system that would cost about M\$ 0.5 (just in plumbing), so we will disregard this approach for the time being.
2. **Transporting bottled gas from surface:** To maintain purity and replenish losses from leaks, a continuous transport of bottled gas will be necessary. A potential additional problem would be the radioactivity brought in with the gas. This would require constant monitoring. Because of these problems it would seems desirable to produce the cover gas *in situ*, from the normal cavity atmosphere . This would eliminate both problems. An estimate of the cost of only one filling cycle of industrial grade of Ar is of about K\$ 20.
3. **Dry Ice:** one interesting possibility we explored was to use CO₂ as a cover gas, transported as a solid (dry ice). The cost of 1 kg of dry ice is about \$0.60, so that the cost per cycle (to fill the volume once, $V_i \sim 7 \text{ m}^3 \sim 14000 \text{ kg}$) would be approximately \$8400. This seems a reasonable expense. We would estimate that during the filling we may use 3 to 4 times this amount. One problem with this gas is the fact that CO₂ tends to readily dissolve in water. In the laboratory test we have conducted, we found that in one day of exposure to CO₂ at approximately 1 At. and at T=10°C, the pH of the water is 4. This value may pose serious problems in terms of corrosion of materials. Therefore we are working to find more satisfactory solutions.
4. **Liquid Air machine:** What is interesting about this approach is that by doing a distillation of N₂ we could also reduce the amount of Rn in the air since the boiling point for Rn is T=211 K, and those of N₂ and O₂ are T=77.35 K and 90.18 K respectively. The disadvantage of this process is that a Liq. N₂ machine is expensive (K\$ 130 for the smallest ~10 l/h) and requires frequent maintenance. It has difficulty with operating on a continuous basis and there have been instance in which leaks have led to suffocation.
5. **Pressure Swing Adsorption (PSA), molecular sieve adsorbent:** This approach may be one that deserves particular attention. Here it is possible to separate the oxygen and nitrogen without using cryogenics. The nitrogen can be produced very pure at 99.99%, in relatively large rates of 2.5 to 10 m³/h and at a reasonable cost (a 2.5 m³/h cost about 20 K\$, a 5.5 m³/h 30 K\$ and a 11 m³/h 40 k\$). Furthermore these machine can operate on a continuous basis for extended periods of

time with minimum maintenance.

Preliminary Conclusions:

In figures 2 and 3 we show the calculation of the amount of O_2 in water as a function of time for a PSA machine that produce $2.5 \text{ m}^3/\text{h}$. The operation of these machine is such that at the nominal rate of $2.5 \text{ m}^3/\text{h}$, the purity of the gas is 99.5%, at half this rate the purity is 99.95% on. Therefore the protocol of operation is as follows; when the purity in the cavity atmosphere is about 90% of the inlet purity, we reduce the influx rate by a factor of 2. In this test no account is taken for leaks, the only assumption is the there is gas flowing out at the same rate that it is flowing out. In figure 4 and 5 we show the same results with the cover gas recirculating for one month prior to the beginning of water filling.

In figure 6 to 10 we present the same results for a machine of $5.6 \text{ m}^3/\text{h}$. In all cases we see that during the first 4 to 5 month there is not a considerable decrease of the amount of O_2 dissolved in water (assuming equilibrium condition, i.e. the amount of O_2 in water is calculated using Henry's law). At the end of the 6.5 month we see a drastic reduction of O_2 of about 4 orders of magnitude. The effect of having the cover gas recirculating for a month prior to filling is not very important to this effect.

This technique may be feasible and economically convenient, the final type of machine (rate produced) will have to be designed according to the expected leaks in the cavity.

We should add that this design would require the use of to separate dryer to remove the H_2O and D_2O form the gas in the cavity atmosphere. Also one could think in using a activated carbon bed to remove some of the Rn in the influx of N_2 . Bhaskar Sur has discussed this interesting possibility in his consideration on cover gas. This possibility seems to be very appealing. Finally there are some reservations that we still have for using this approach, it is related to the possibility that the molecular sieve may contain unacceptable amounts of Ra . To explore this possibility we have arranged with one of the suppliers of the PSA machine (Nitrotech) to provide us with two samples of about 1 kg each of the molecular sieve (made out of small pellets). The two samples would come from the same production batch, one would be unused in the machine (virgin sample) and the other would have been use for about a month continuously prior to been send to us. At Guelph P.Jagam will measure the activity of the two samples looking for traces of Ra and Rn . In the best scenario, the sample used in the machine would contain a larger activity of Rn that will decay in few days. These test we think will be crucial for the final selection.

Appendix I

Properties of Air and its components.

Element	% in Volume	M[AMU]	T _{boiling} [K]	ρ [g/l]	At. radii[pm]
N ₂	78.084	28.01	77.35	1.259	65
O ₂	20.946	32.0	90.18	1.251	60
CO ₂	0.033	44.0	196.0		
Ar	0.934	39.95	87.3	1.784	95
Ne	18.18e-6	20.18	27.09	0.901	70
He	5.24e-6	4.0	4.2	0.1787	50
Kr	1.14 e-6	83.8	119.	3.74	110
Xe	0.087e-6	131.3	165.0	5.89	130
H ₂	0.5 e-6	2.0	20.27	0.0899	25
CH ₂	2.0 e-6	14.0			
N ₂ O	0.5e-6	30.0			
Rn		222.0	211.0	9.91	190

Appendix II

More Properties of Air and its components.

Element	% in Volume	Henry's const. $\mu\text{g}(\text{gas})/\text{g}(\text{H}_2\text{O})$	At. Ionz. Pot.[ev]
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at 1 at

N ₂	78.084	13	14.0
O ₂	20.946	8.61	13.1
CO ₂	0.033	1517.	
He	5.24e-6	1.48	23.7
Ne	18.18e-6		20.8
Ar	0.934		15.2
Kr	1.14 e-6		13.5
Xe	0.087e-6		11.7
Rn			10.4
H ₂	0.5 e-6		13.1
CH ₂	2.0 e-6		
N ₂ O	0.5e-6		

Amount of O₂ and N₂ in disolv. H₂O (EQ)

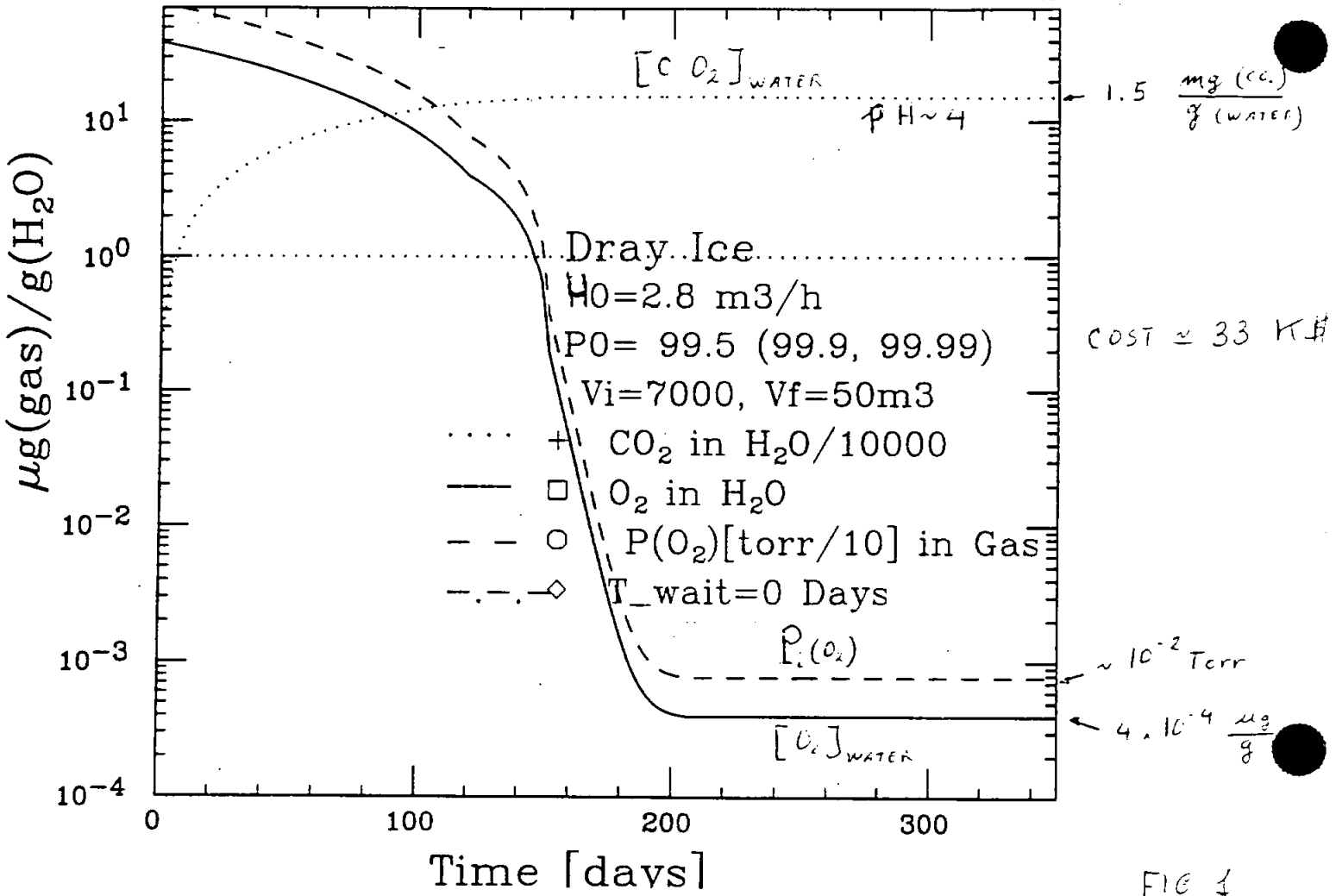


FIG 1

Percentage of N2 in Cover Gas

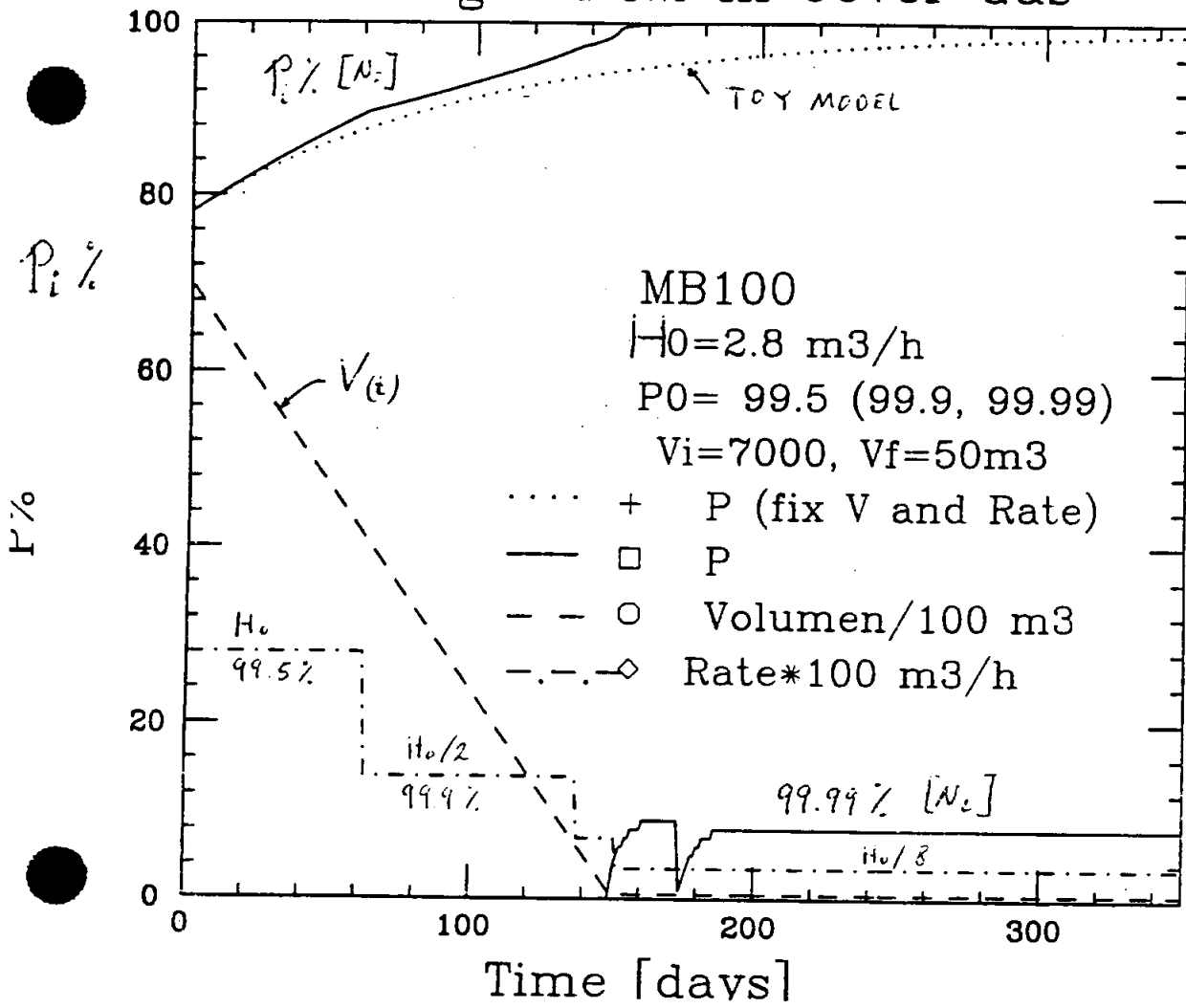
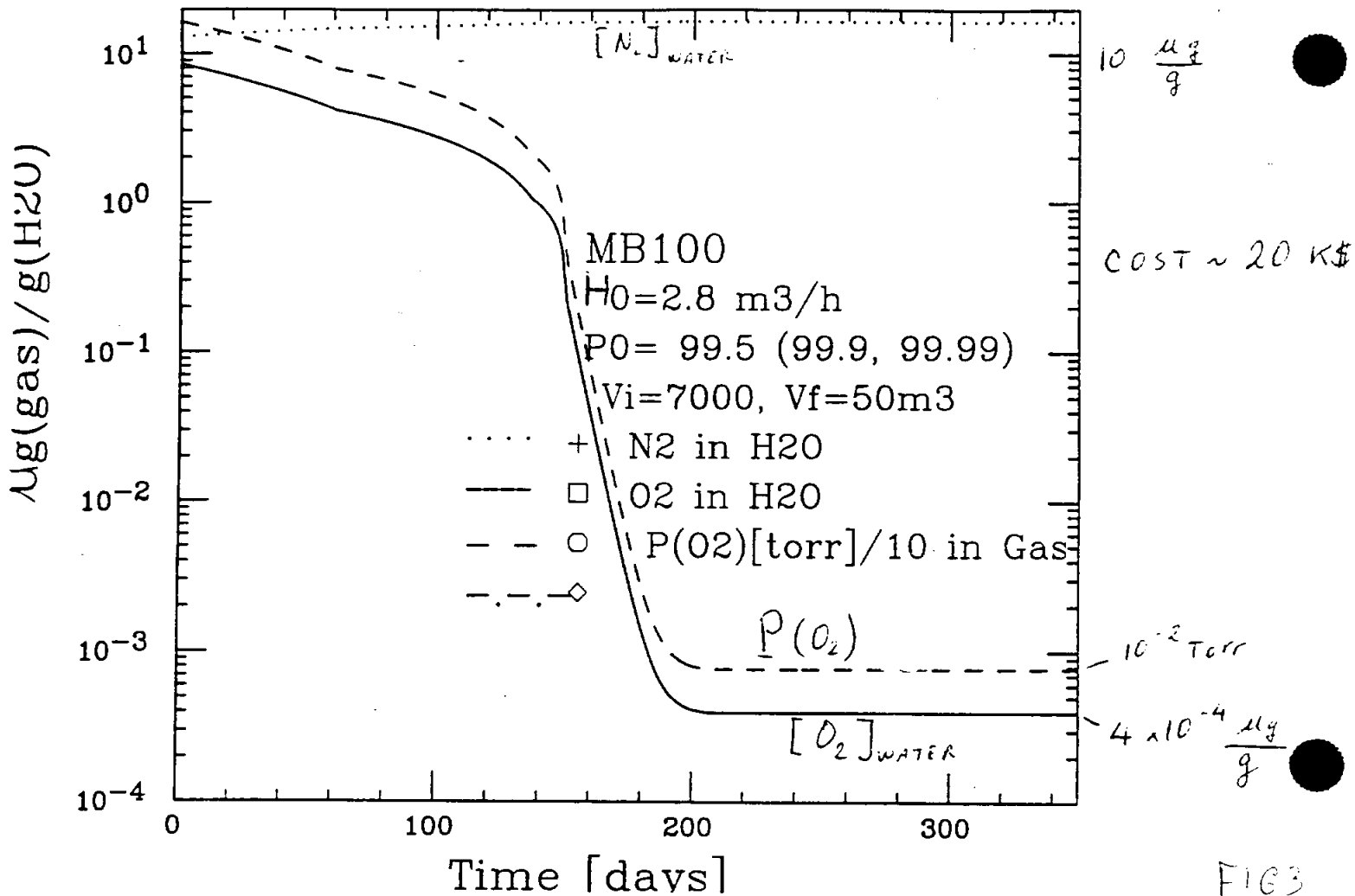
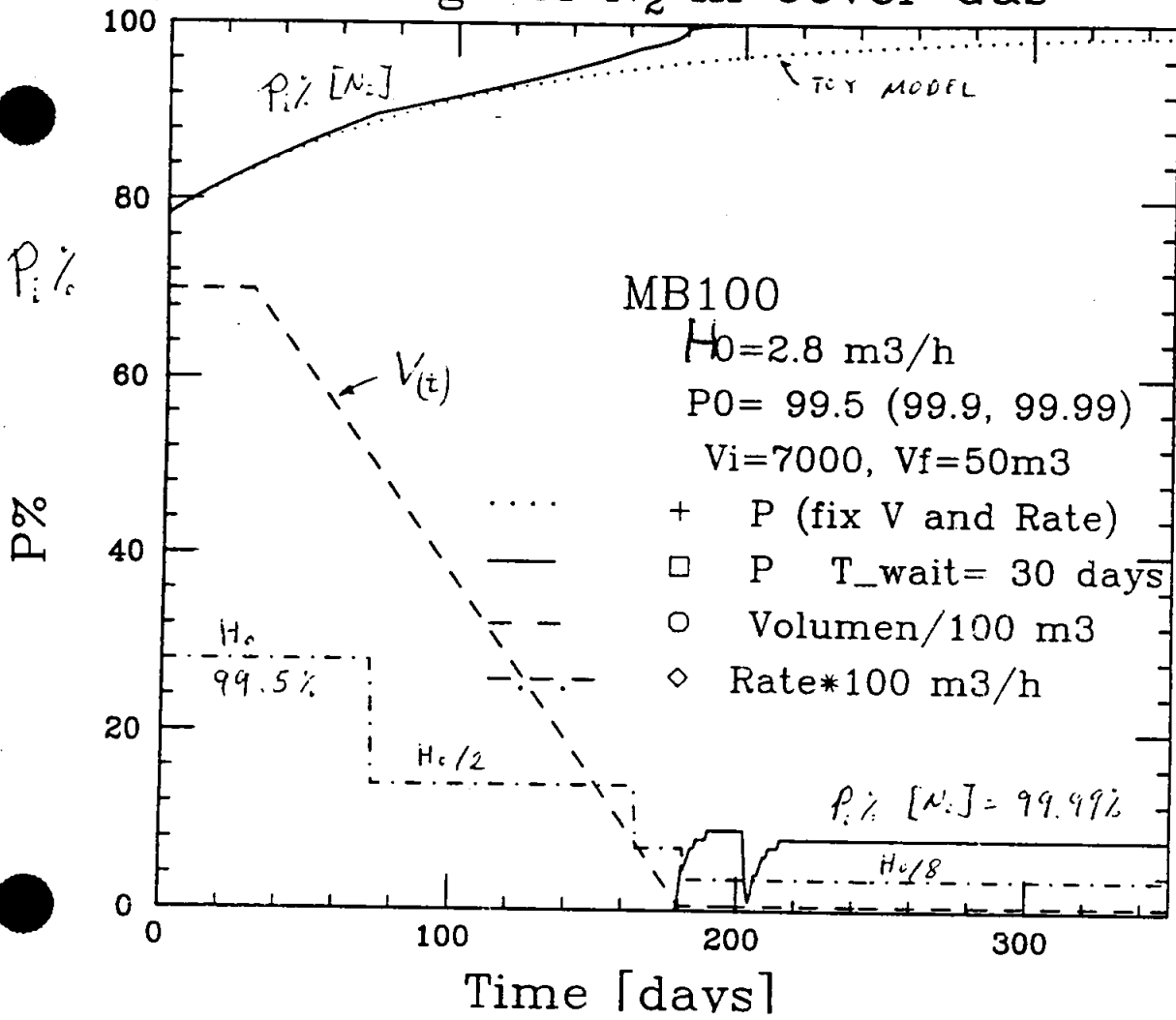


FIG 2

Amount of O2 and N2 in disolv. H2O (EQ)



Percentage of N₂ in Cover Gas



COST ~ 20 K\$

FIG. 4

Amount of O₂ and N₂ in disolv. H₂O (EQ)

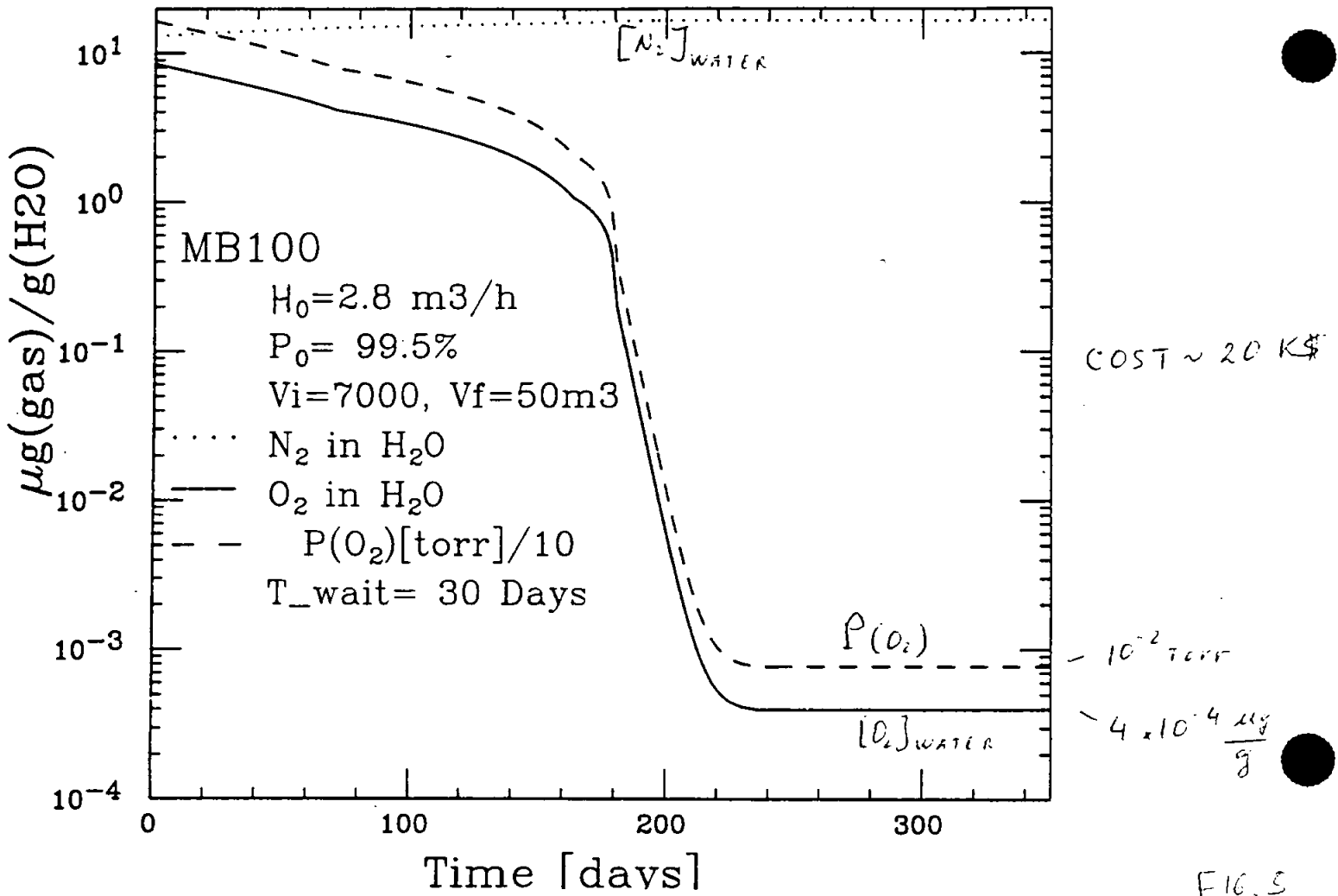


FIG. 5

Percentage of N₂ in Cover Gas

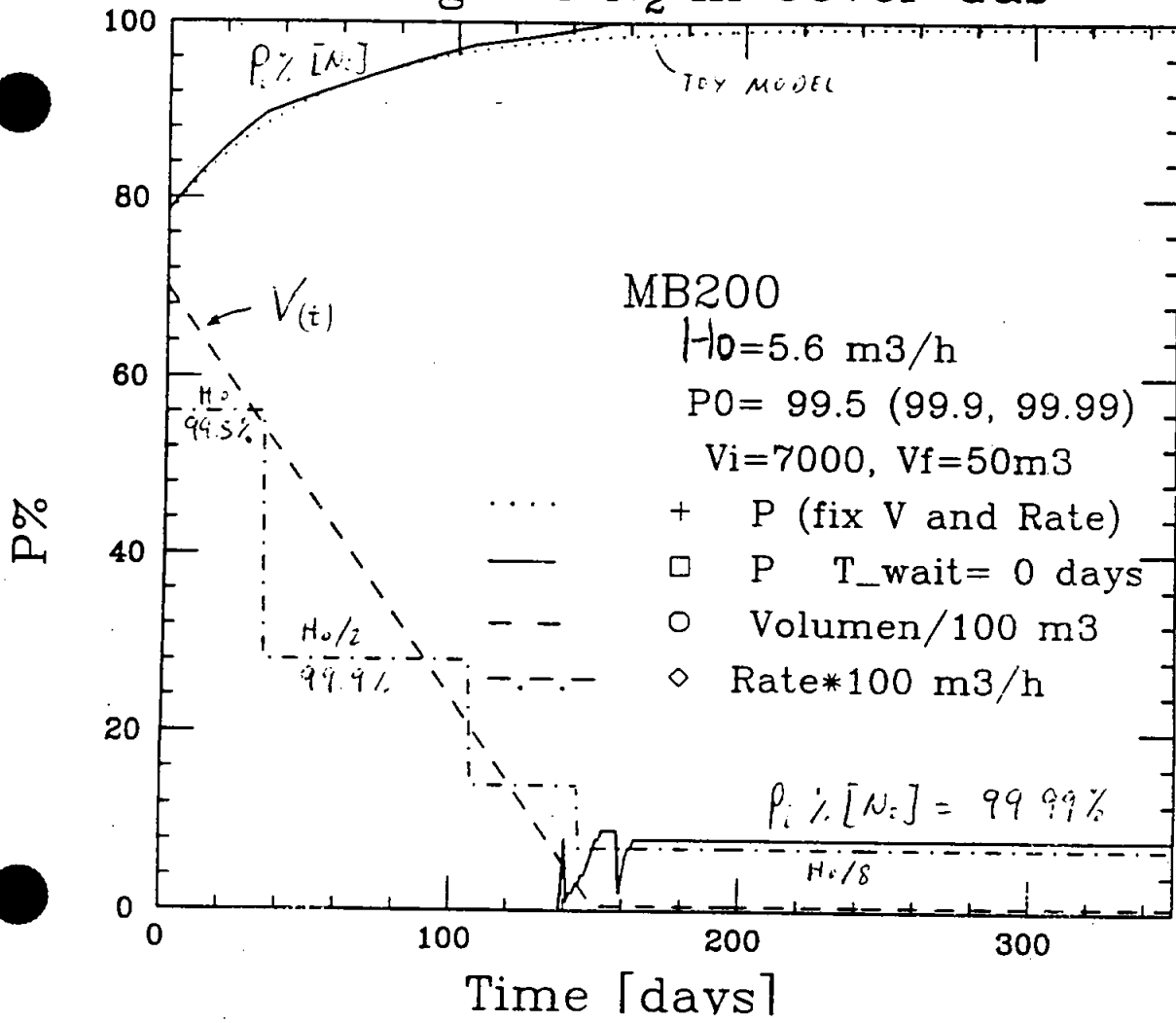


FIG. 6

Amount of O₂ and N₂ in disolv. H₂O (EQ)

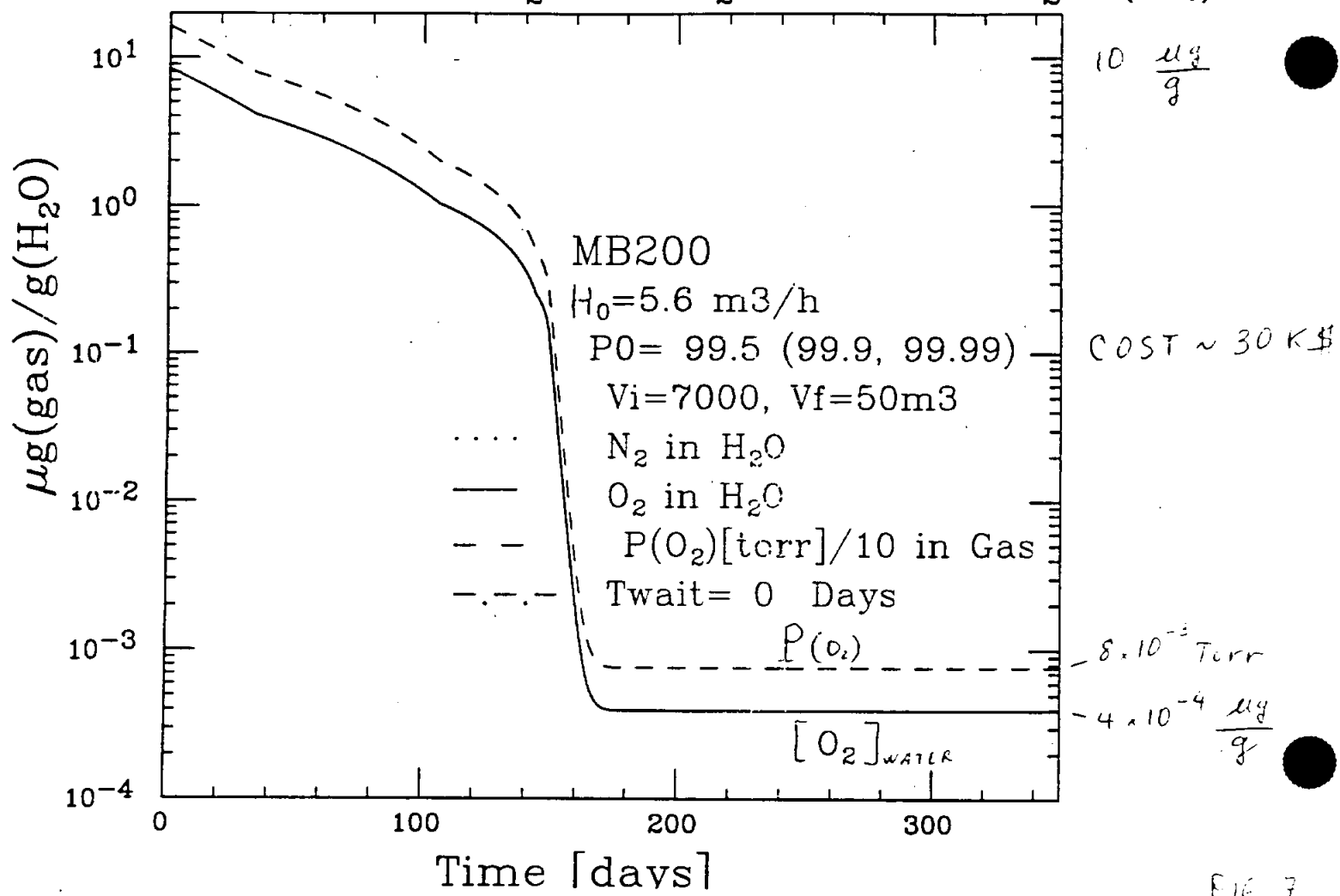


FIG. 7

Percentage of N2 in Cover Gas

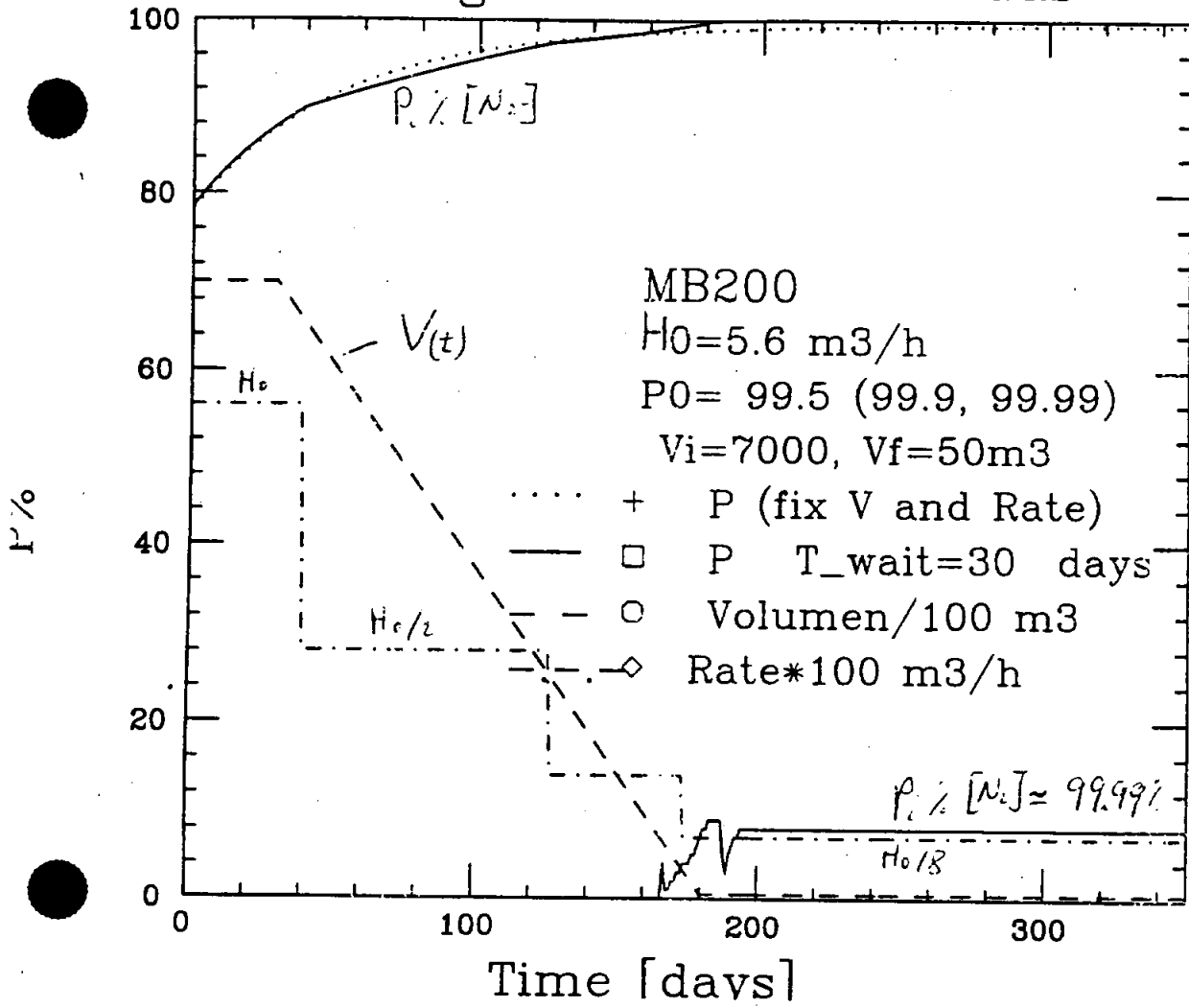


FIG. 8

Amount of O2 and N2 in disolv. H2O (EQ)

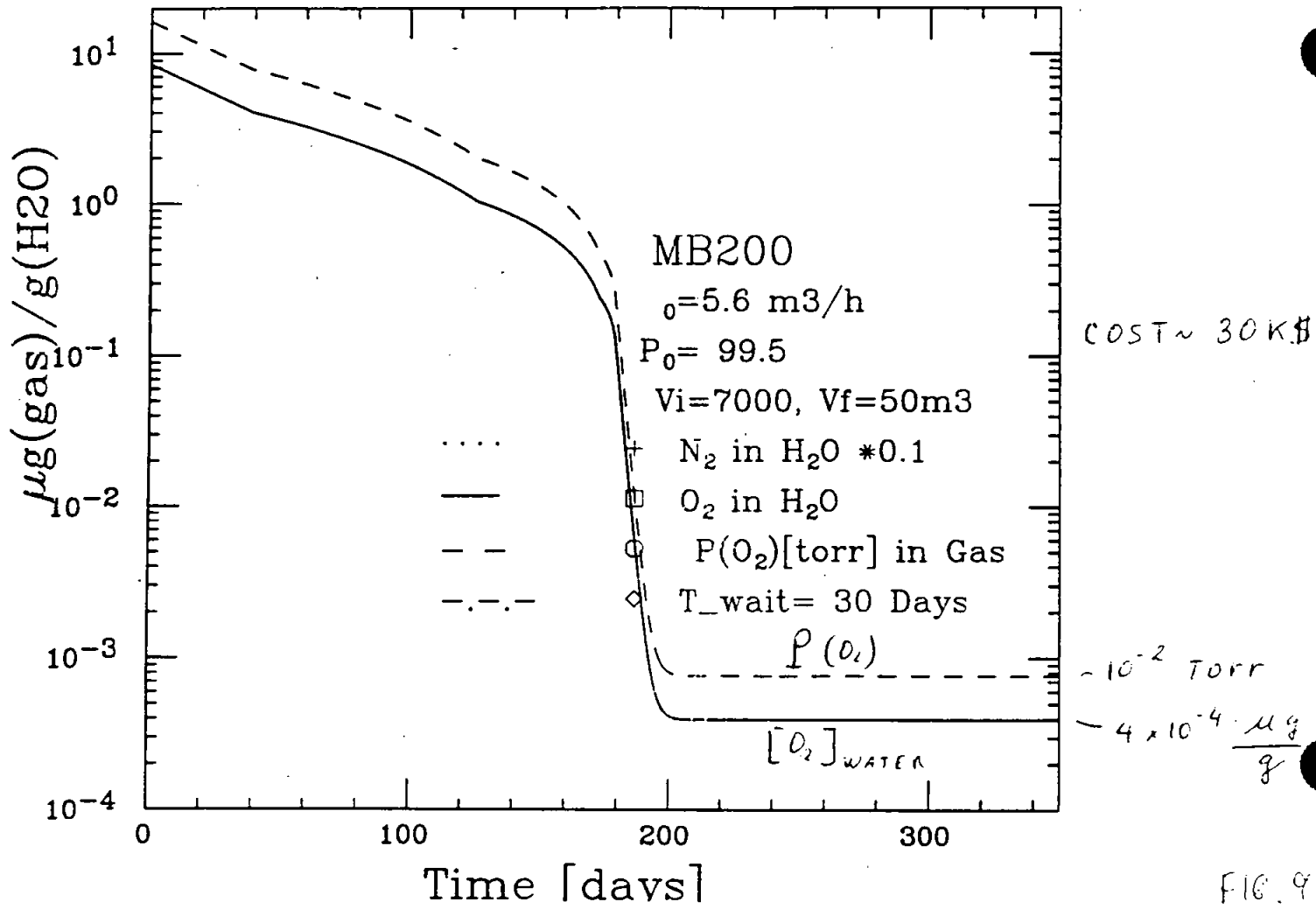


FIG. 9

A NOTE ON BIO-OPTICS

Chris Wellham
28 Feb 92

- $\leq 10^6$ cells/ml : clear water
 $\sim 10^7$: bugs on edge of visibility
 $\sim 10^8$: visible bloom
 $\sim 10^9$: milky

E-coli is limited by ambient O_2 at $\sim 10^8$ cells/ml

Aerobic D_2O + plastics $\sim 10^4$ cells/ml

Anaerobic H_2O " $\sim 10^4$ (Medigas) $\sim 10^6$ (Ar) cells/ml

Anoebic H_2O " $\sim 10^7$ cells/ml

\therefore we guess that a reduction of ambient O_2 by
2 or 3 orders of magnitude would reproduce
laboratory anaerobic conditions.

Initial results \Rightarrow aerobic D_2O better than anaerobic H_2O .

$(1\text{cm})^3$ cell of 10^8 e-coli \approx one scattering length at 375nm^*

So, if we had 10^4 cells/ml in D_2O (more likely a bio-film),

$r_{AV} = 600\text{cm} = 6\%$ of a scattering length

N.B. Uniform bio-film probably more benign :

* Nucleic acids &
proteins only
absorb $< 300\text{nm}$