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RAPHAEL *(ReActor for Process heat, Hydrogen And ELectricity generation)*

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Document title

Aqueous phase ingression into non-irradiated graphite

Executive summary

The graphite matrix is the first barrier against the intrusion of water into an HTR pebble fuel element. Therefore the take-up of water and the penetration depth is an important information for the development of a long term behaviour model.
The obtained results show, that a dummy fuel pebble can take-up about 10 ml solution and the solution is homogeneous distributed in the graphite matrix.

Revisions

Rev.	Date	Short description	Author	WP Leader	SP Leader	Coordinator
00	dd/mm/yyyy	First issue	Name, Organisation	Name, Organisation *Signature*	Name, Organisation *Signature*	Name, Organisation *Signature*
01	31.10.2006	Draft issued	Fachinger, FZJ	Fachinger FZJ	Von Lensa FZJ	
02	30.01.07	2. Draft	Fachinger, FZJ	Fachinger FZJ	Von Lensa FZJ	
03	15.05.07	Final Version	Fachinger, FZJ	Fachinger FZJ	Von Lensa FZJ	E. Bogusch FANP

Aqueous phase ingression into non-irradiated graphite

1 Description of the experimental set up

1.1 Water ingression

A sketch of the experimental set up is shown in Figure 1. A graphite pebble is placed in the spherical flask, which consists of two half spheres. The half spheres are fixed together by a metal clamp (Figure 2). The valve 1 above the spherical flask allows the evacuation of the flask. Three test series have been performed with different pressures, which could be adjusted by valve 3.

1. 400 mbar / 0.1 M NaCl
2. 40 mbar / water
3. 2-4 mbar / 0.1 M NaCl

When a stable pressure is adjusted the valve 2 below the flask is opened and the flask is filled with 0.1 M sodium chloride solution or water up to the specified mark. The volume of the solution is measured with the burette. Then the vacuum pump is shut down to establish atmosphere pressure in the flask. The valve 2 is opened again and the flask is filled up again with solution to marked level. The used volume up to this step had been noticed after 1 minute as initial volume V_i. The further water penetration into the pore system of the graphite pebble is compensated again in defined time periods. These additional volumes were noticed as V_t.

1.2 Chloride distribution in the graphite pebble

The pebbles are dried in a furnace at 110°C after the ingression experiments and 10 layers of five 2 mm wide graphite stripes are chipped from the graphite by a lathe. The depth of the layers is shown in Figure 3. The graphite chips obtained from the 5 stripes of one layer are mixed and leached in boiling water for 5 hours. The chloride concentration is determined in the filtrate by UV/VIS spectrometry.

2 Description of the graphite pebbles

The graphite pebbles had been obtained from an experimental facility, which tested the moving behaviour in an HTR core. Two different types of graphite pebbles had been used in these former experiments, A3-3 graphite and the advanced graphite matrix A3-27. No information was available which type of graphite pebbles was in the obtained transport drum. Following parameters had been determined:

Diameter: 5.95 ± 0.1cm

Mass: 194,5 ± 0,25g

Furthermore the oxidation rate has been measured by thermo-gravimetry to determine the graphite type (Figure 4). The shape of the measured oxidation rate curve is similar to well-defined A3-3 graphite. The different height is probably related to up-take of metal impurities and other damages during the moving experiments. The obtained results indicate that the used graphite type is A3-3, which is also more probable because the used amount of A3-3 pebbles was at least two orders of magnitude larger than pebbles made of A3-27.

A first experimental series shows a large scattering of the amount of water in the graphite pores. This could be related to dust on the surface and in the larger pores. Therefore the pebbles were cleaned for further experiments in an ultrasonic bath with ethanol. After cleaning they were dried in a furnace at 90°C. About 80 mg of graphite dust is removed by this cleaning procedure.

3 Results of ingression experiments

The first series of ingression experiments were performed with non-cleaned graphite pebbles. The take up of water is nearly completed within 2 hours with a mean water amount of 9.5 ml. A additional take-up of 1 ml solution can be achieved after 16 hours (Figure 5). The experiments with non-cleaned graphiteshow a wide scattered take-up of sodium chloride solution from 1.3 to 10.3 mL after one hour (Figure 6) with an mean value of 6 mL. The Figure 7 shows the distribution of the number of pebbles related to the water up-take in steps of 0.5 mL. No clear defined maximum could be obtained from this figure. These changes after an ingression time of 16 hours. The mean value of the water up-take is increased to 8.25 mL and the distribution curve shows a clear maximum in this area. This wide scattering of the water up-take could be explained by the history of the pebbles. The pebbles had been used for experiments to study their movement in a HTR reactor core. Graphite was rubbed off from the surface of the pebbles during these experiments and fine graphite dust has clogged some surface pores. Therefore further experiments were performed with cleaned graphite pebbles. The Figure 8, Figure 10 and Figure 12 show the results of the water ingression into cleaned pebbles at 2, 40 and 400 mbar. The scattering of the water up-take is reduced in these experiments series in comparison to the non-cleaned pebbles. The following Table 1 shows the mean values of the ingression experiments at 2 mbar, 40 mbar and at 400 mbar. The mean values of the water take-up are compatible at the different pressures. However the standard deviations at 40 and 400 mbar are smaller in comparison to the series at 2 mbar. This can also be seen in the distribution of the number of pebbles related to the water up-take (Figure 9, Figure 11, Figure 13). The experimental series at 2 mbar shows only a significant maximum at the instantaneous water take-up after 1 minute. The experimental series at 400 mbar shows significant maxima at all times whereas the amount of penetrated water becomes more scattered in the experimental series at 40 mbar.

Table 1: Take-up of water at different pressures

Pressure	2 mbar		40 mbar		400 mbar	
Time (min)	∅ (mL)	Std.dev.	∅ (mL)	Std.dev.	∅ (mL)	Std.dev.
1			1.7	0.2		
5	4.9	0.7	5.1	0.2	6.1	0.6
10	6.3	1.2	6.4	0.2	7.3	0.5
30	7.5	1.3	9.3	0.3	8.3	0.5
60	8.3	1.3	10.2	0.6	8.9	0.5
120	8.9	1.2	-	-	9.6	0.4
180	9.1	1.2	10.5	0.6	9.6	0.4
1020	10.1	0.7	-	-	10.3	0.4
1320	-	-	10.7	0.6	-	-

4 Determination of the water distribution in the pebble

The Figure 15 shows the distribution of chloride in a pebble after drying, which was taken up with 11.4 mL of a 0.1 M NaCl solution. The graphite contained about 0.23 mg Cl^- mg/g graphite with a standard deviation of 0.03 except the surface layer. Dependence from the depth could not be observed.

5 Conclusions

The obtained results show, that a pure A3-3 graphite pebble will take up on an average about 10 to 11 mL of water. The uncleaned pebbles show a wide scatter take-up of solution after one hour and an average water take-up of about 8 to 9 mL after 16 hours. This is about 3 mL less than the average water take-up of cleaned pebbles. This can be explained by clogging of pores with fine graphite particles. Such an effect can be expected also for spent HTR fuel pebbles. However the clogging is causing larger deviations and smaller amounts of water take-up. This would results in a larger number of examinations to obtain a reliable statistic. Furthermore the larger volumes of penetrated solution are conservative for further considerations. Therefore further investigations will be performed only with cleaned graphite.
However the pore volume of cleaned pebbles still varies in a wide range and the take-up of water differs from 9 ± 12 mL. This scattering of the water up-take increases, when up-take reaches the maximum filling volume.
This average volume of 10.5 mL indicates that the pores down to size of about 1 µm are filled with water (Figure 16). However the pore size distribution was measure with Hg porosimetry, which correlated the pore size with the pressure necessary to fill the pores. But this method can lead to an opening of closed pores and especially the larger volume of pores < 1 µm. Therefore it is not clear whether the pores > 1µm were filled with water or the open pore volume is smaller than indicated by the blue curve in Figure 16 and smaller pores were also filled.
An answer to the question can hopefully be obtained by the following investigations of the pore system:

1. Determination of the open meso and micro pores. Therefore new equipment will be installed at FZJ in the beginning of 2007.
2. Investigation of the pore structure by tomographic methods (Foreseen in the "Minwaste" proposal in FP7.
3. Determination of the water up-take into pebbles, which had been exposed to high pressure. These examinations are proposed for the first half of 2007.

The real HTR fuel pebbles will probably have a pore volume different from pure graphite. Therefore penetration experiments are proposed in 2007with unirradiated spent fuel elements and irradiate graphite.
The investigation of the chloride distribution in a dried pebble shows a more or less homogeneous chloride concentration in the graphite. This indicates that the penetrated solution is homogeneous distributed in the whole pebble and that the open pore system has connections through the whole graphite. However the chloride concentration was only slightly above the initial chloride concentration of the graphite. Therefore these investigations will be repeated with a more concentrated NaCl-solution in the beginning of 2007.

Appendix

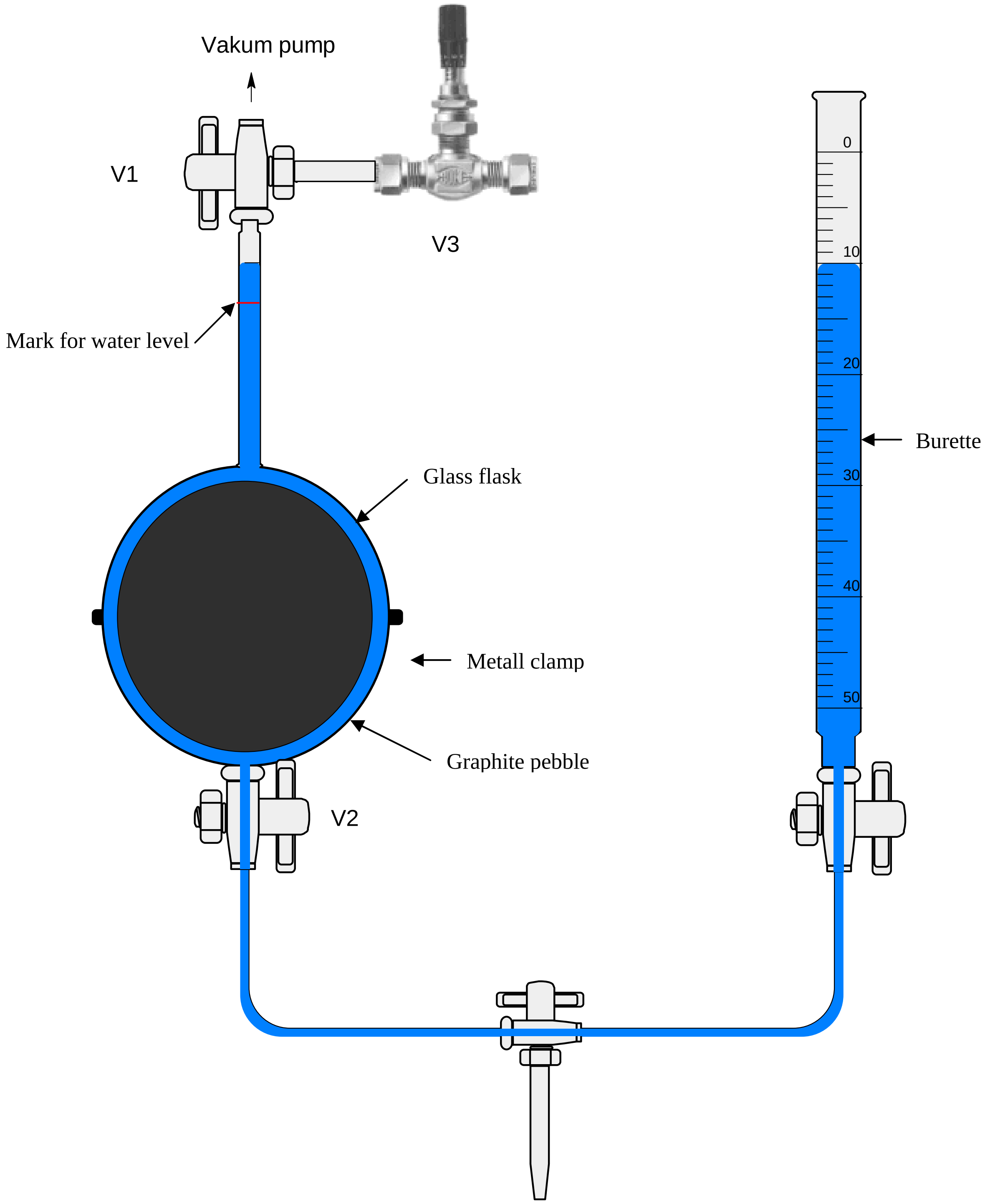

Figure 1 Experimental set up

Figure 2: Spherical flasks with graphite pebbles

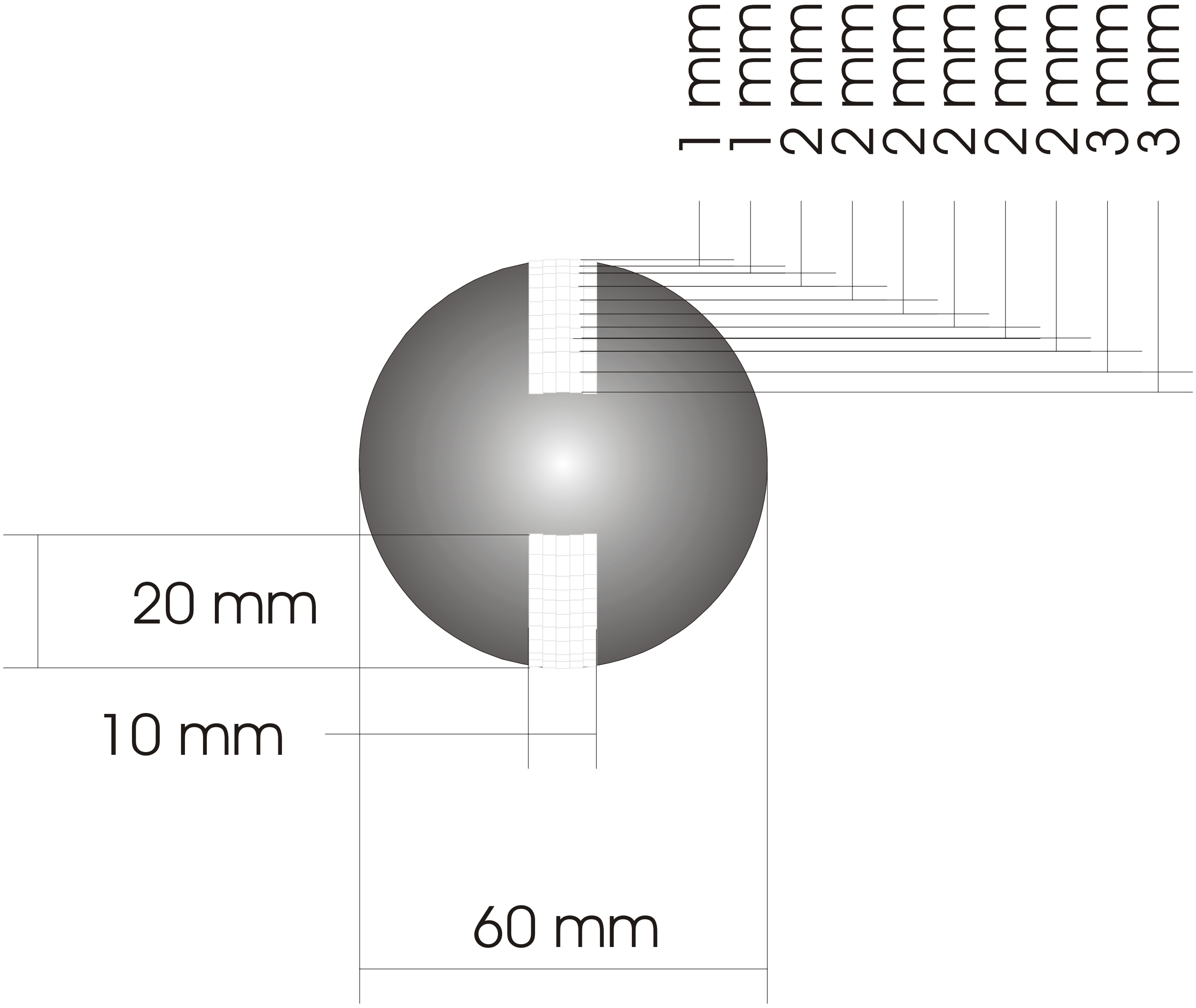

Figure 3: Lathing scheme of the pebble

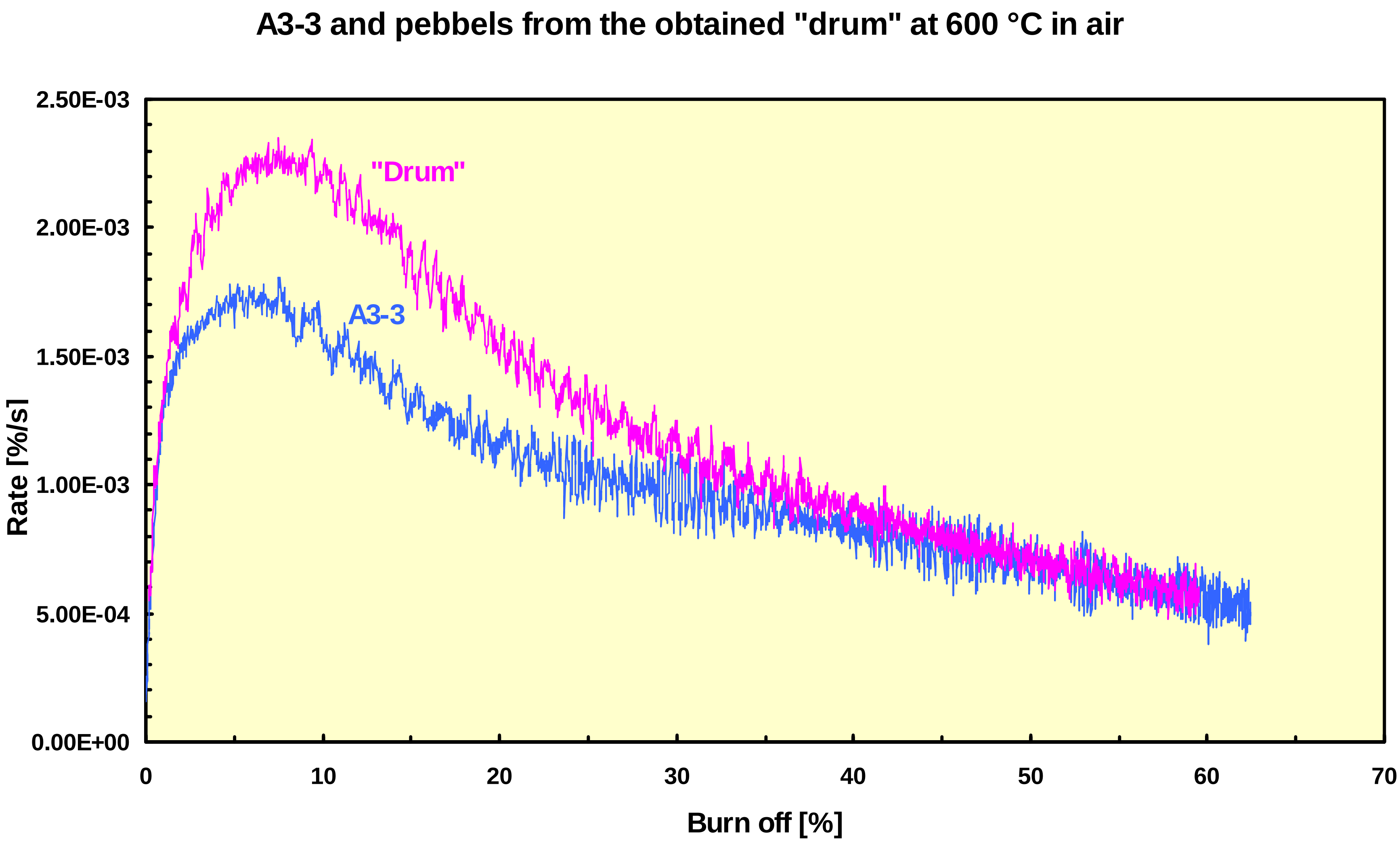

Figure 4: Determiantion of oxidation rates

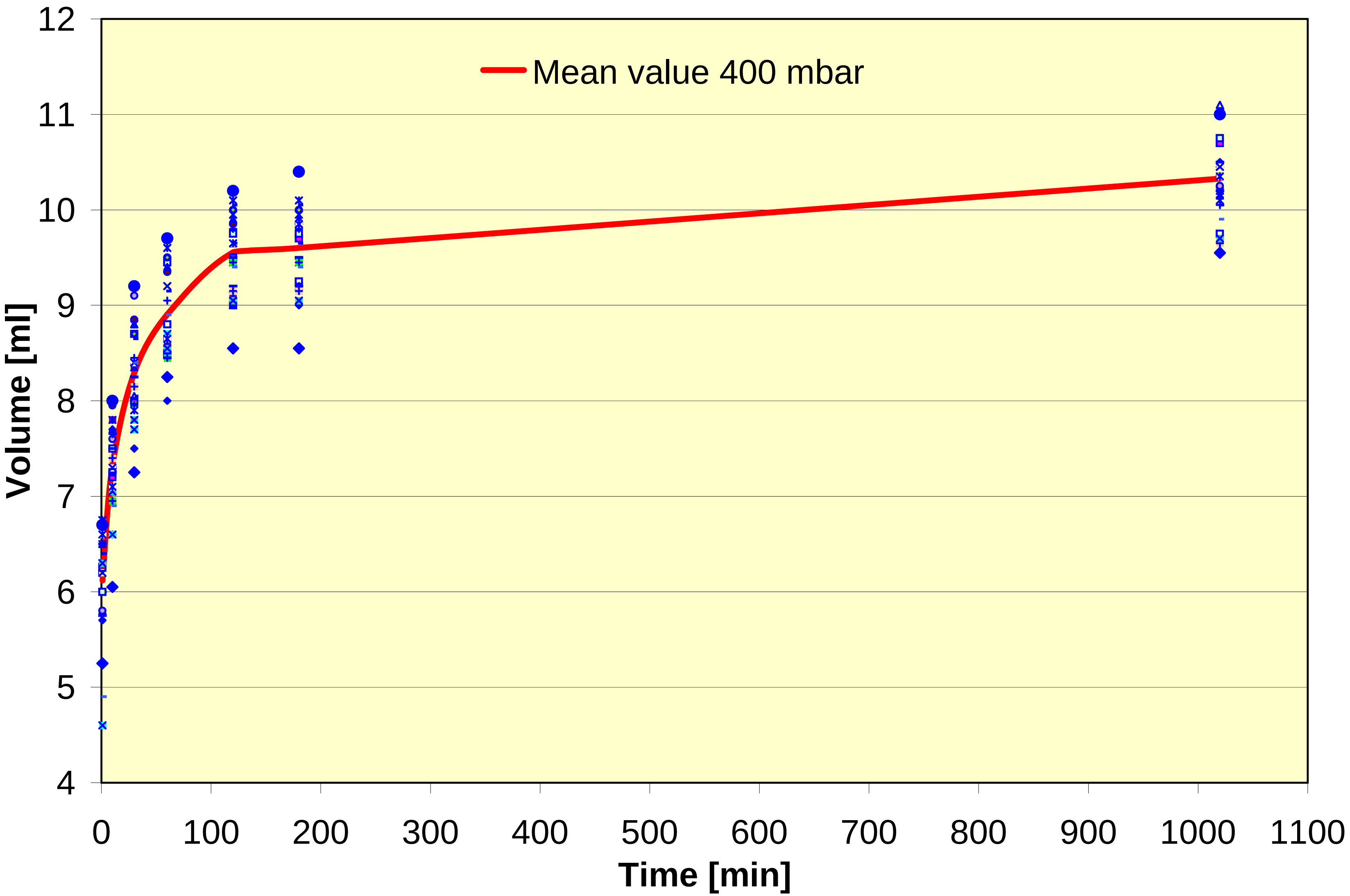

Figure 5: Time dependence of water take-up in non-cleaned graphite pebbles at 400 mbar

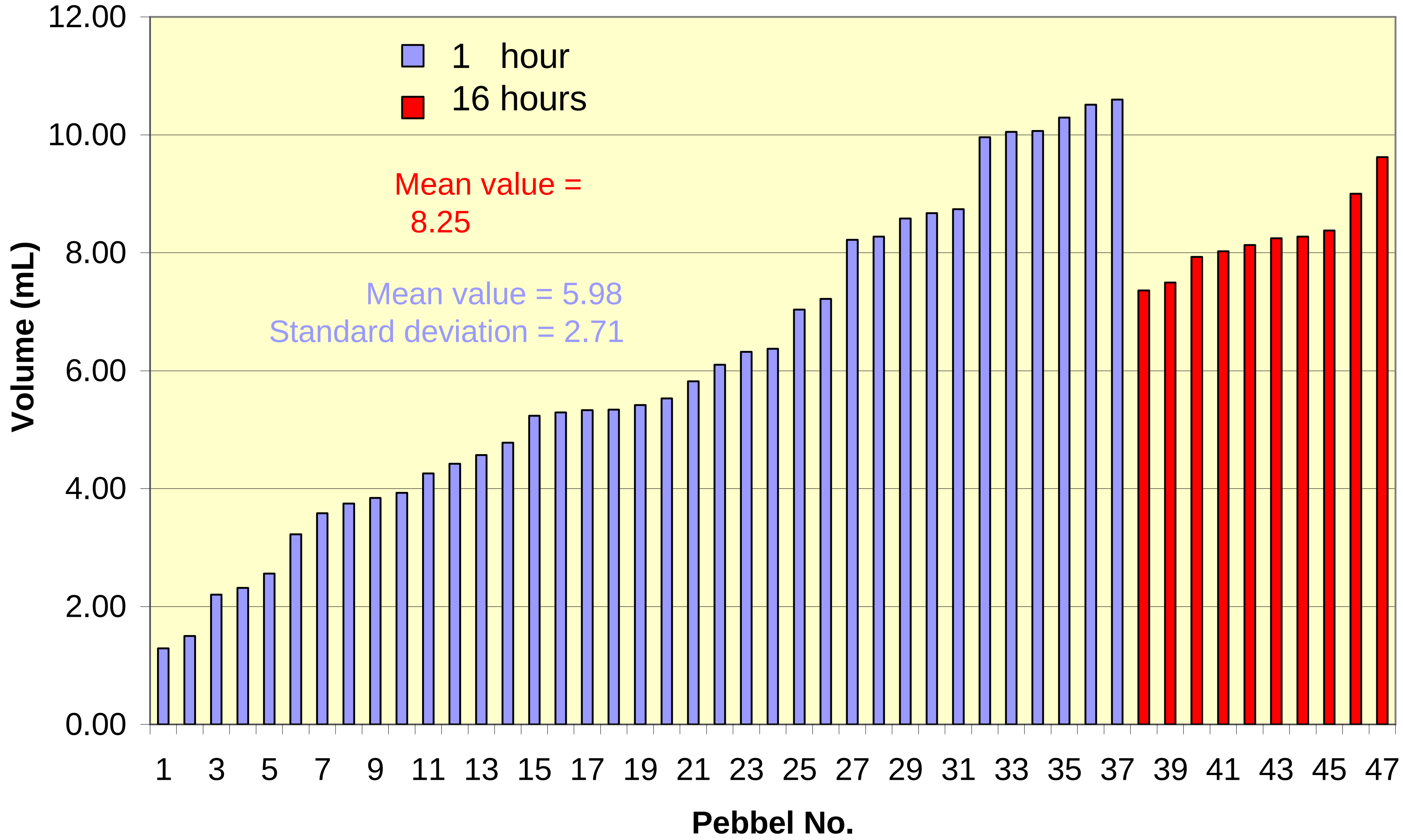

Figure 6: Take-up of water in non-cleaned graphite pebbles at 2 mbar

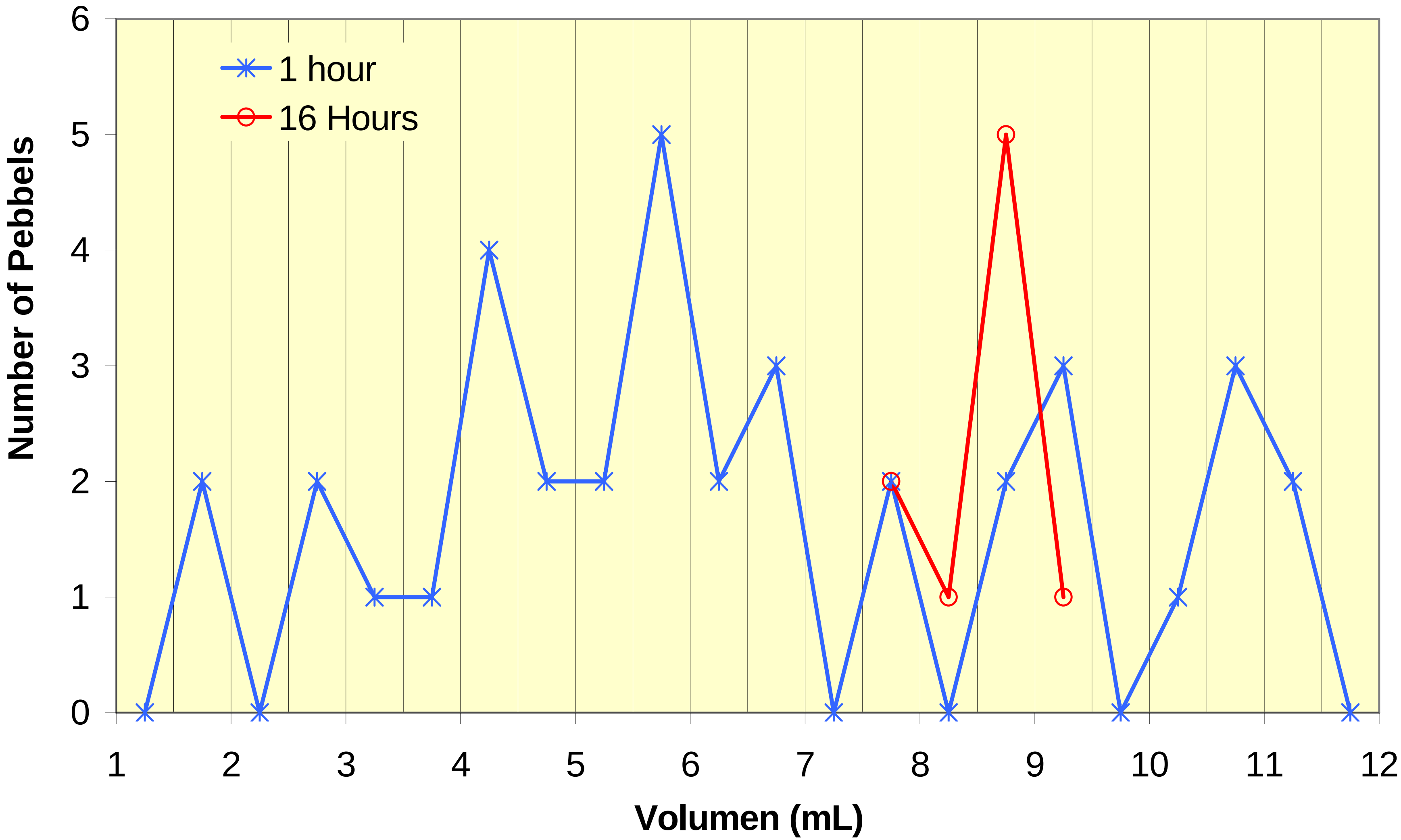

Figure 7: Distribution of the water take-up in non-cleaned pebbles at 2 mbar

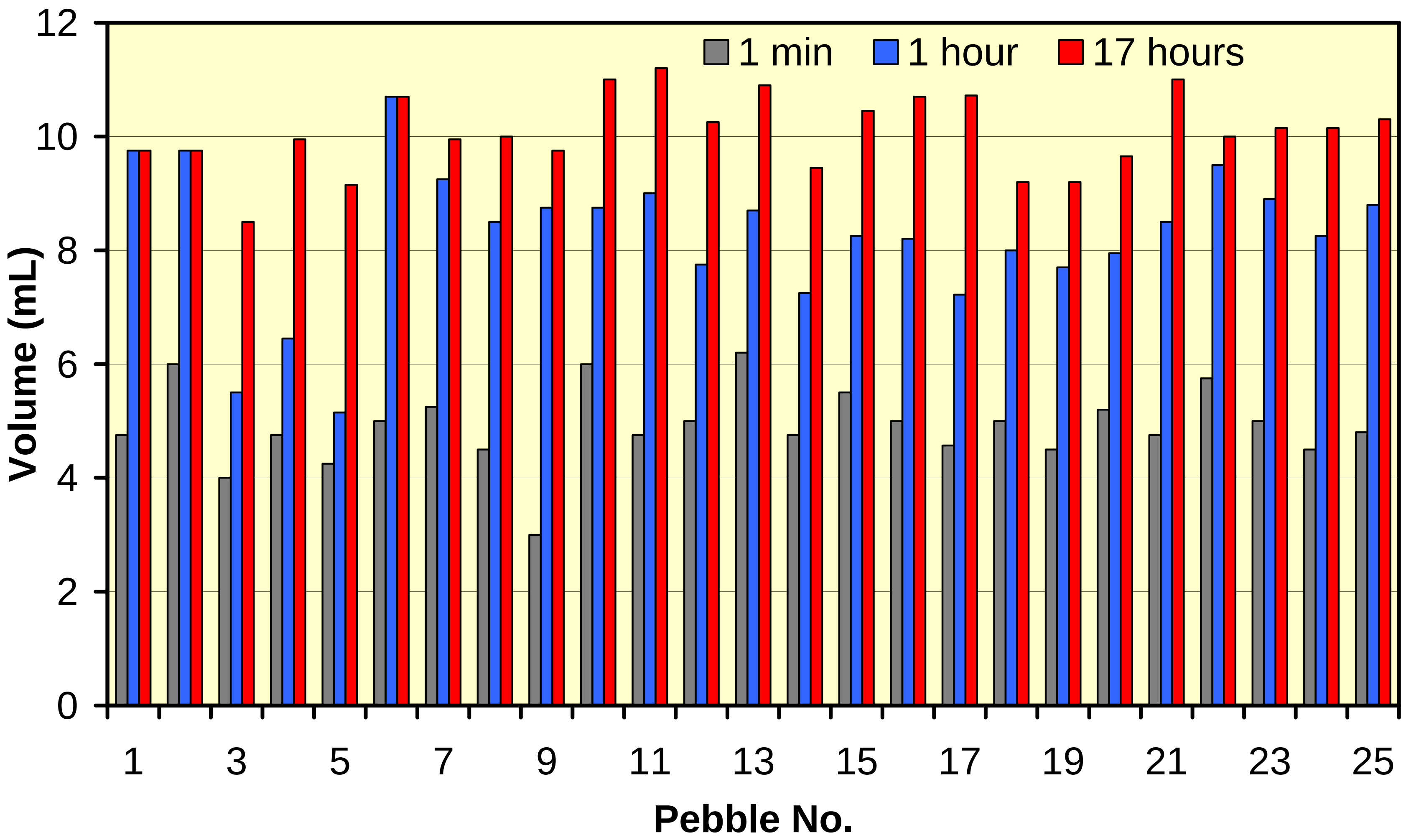

Figure 8: Take-up of water in cleaned graphite pebbles at 2 mbar

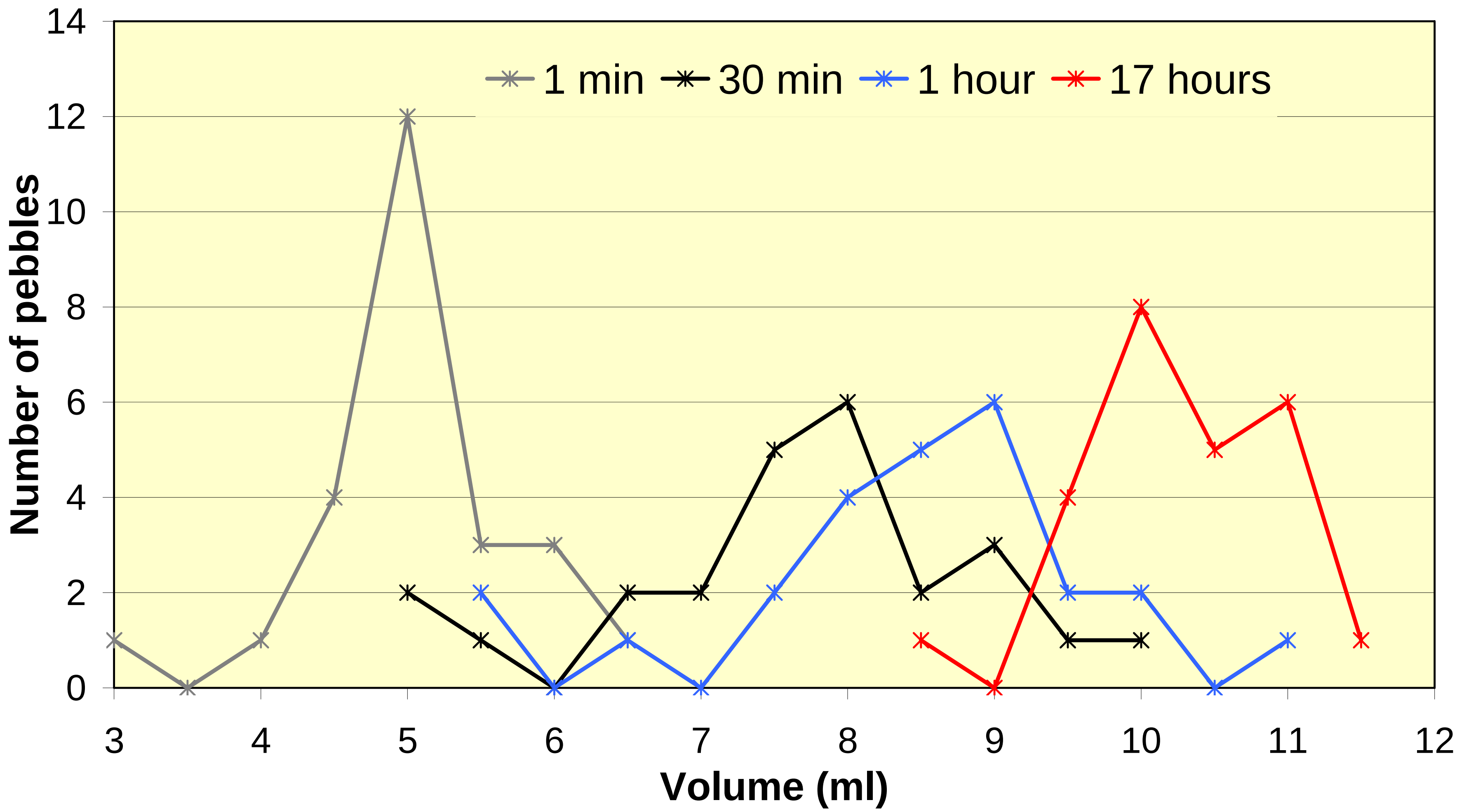

Figure 9: Distribution of the water take-up in cleaned pebbles at 2 mbar

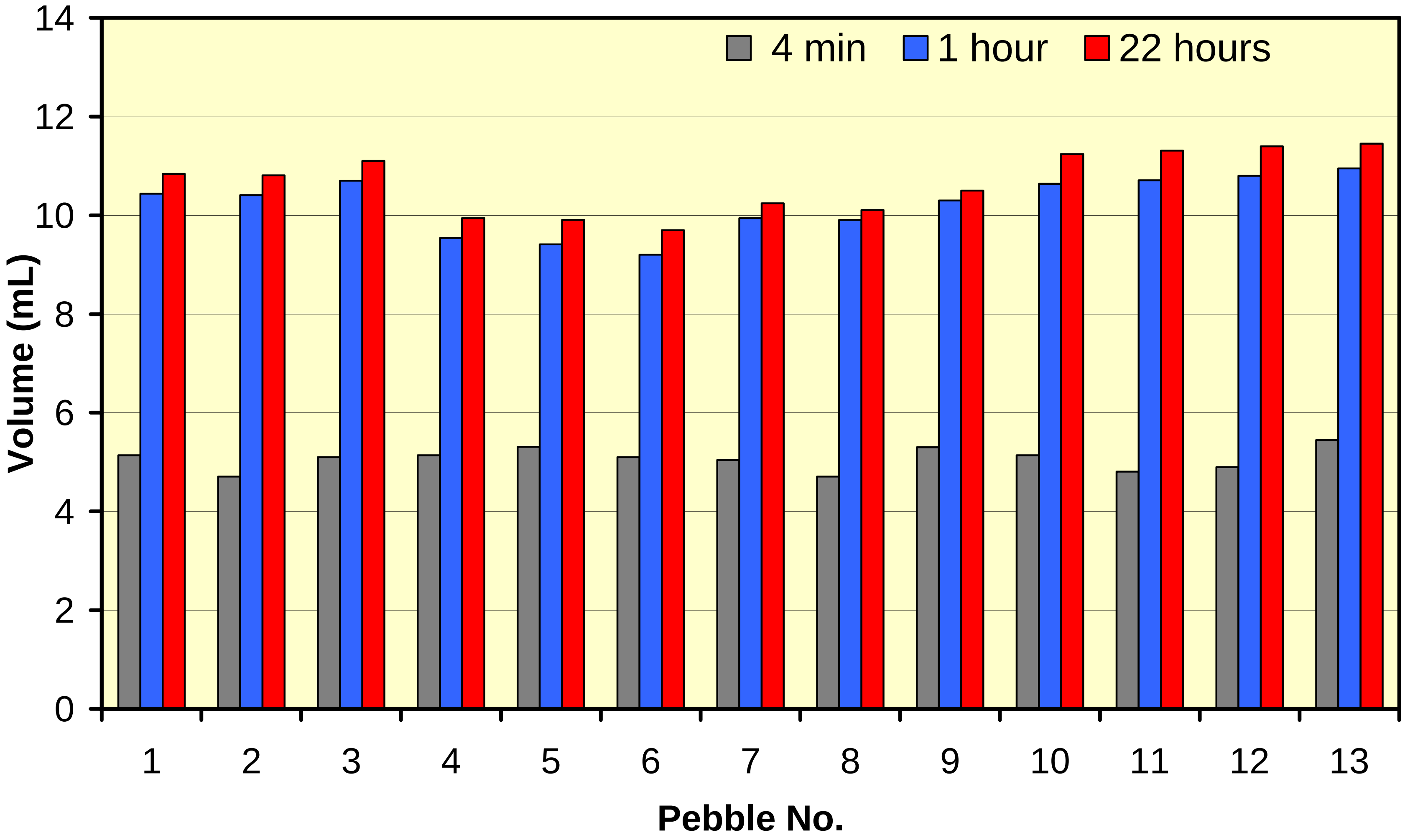

Figure 10: Take-up of water in cleaned graphite pebbles at 40 mbar

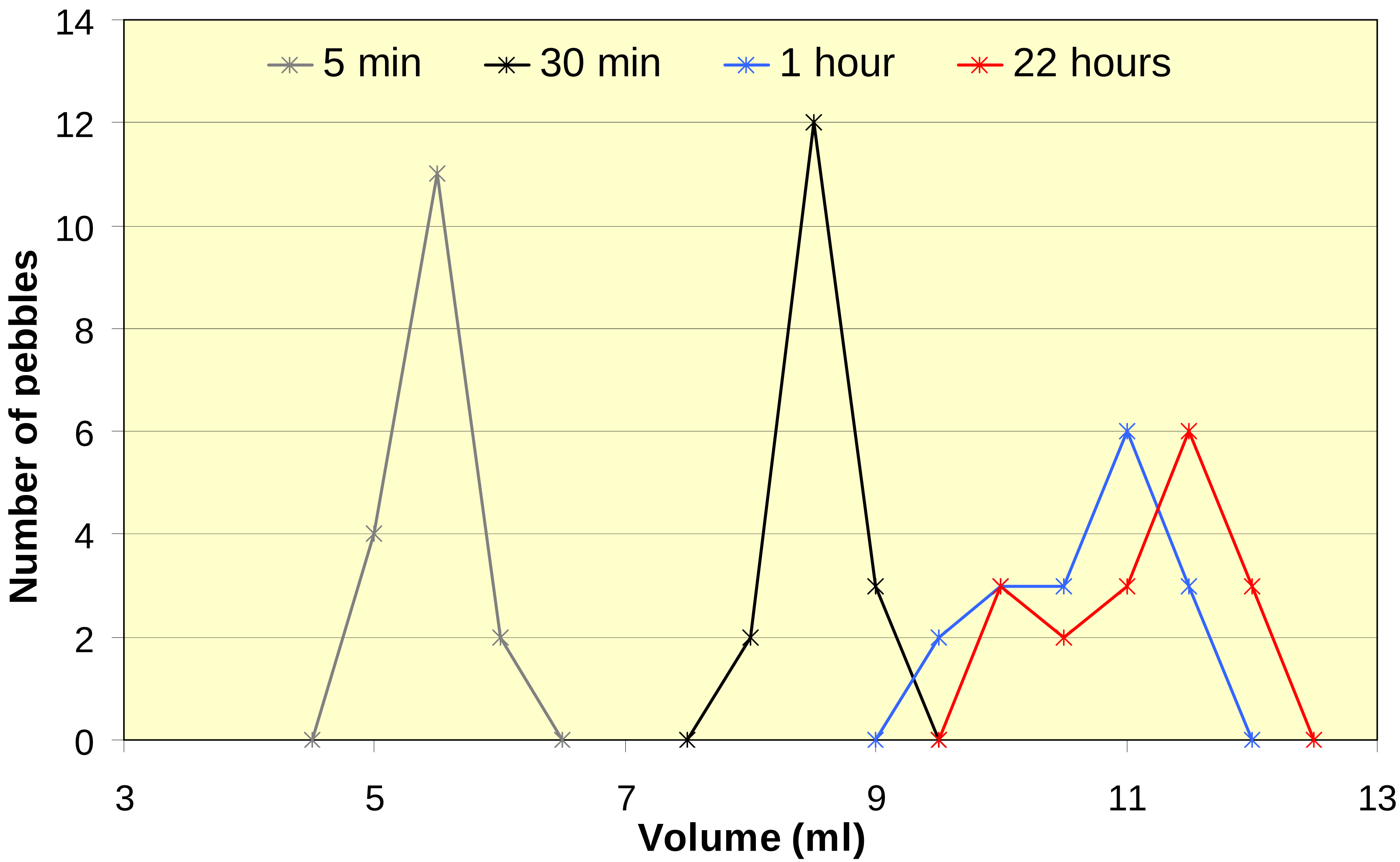

Figure 11: Distribution of the water take-up in cleaned pebbles at 40 mbar

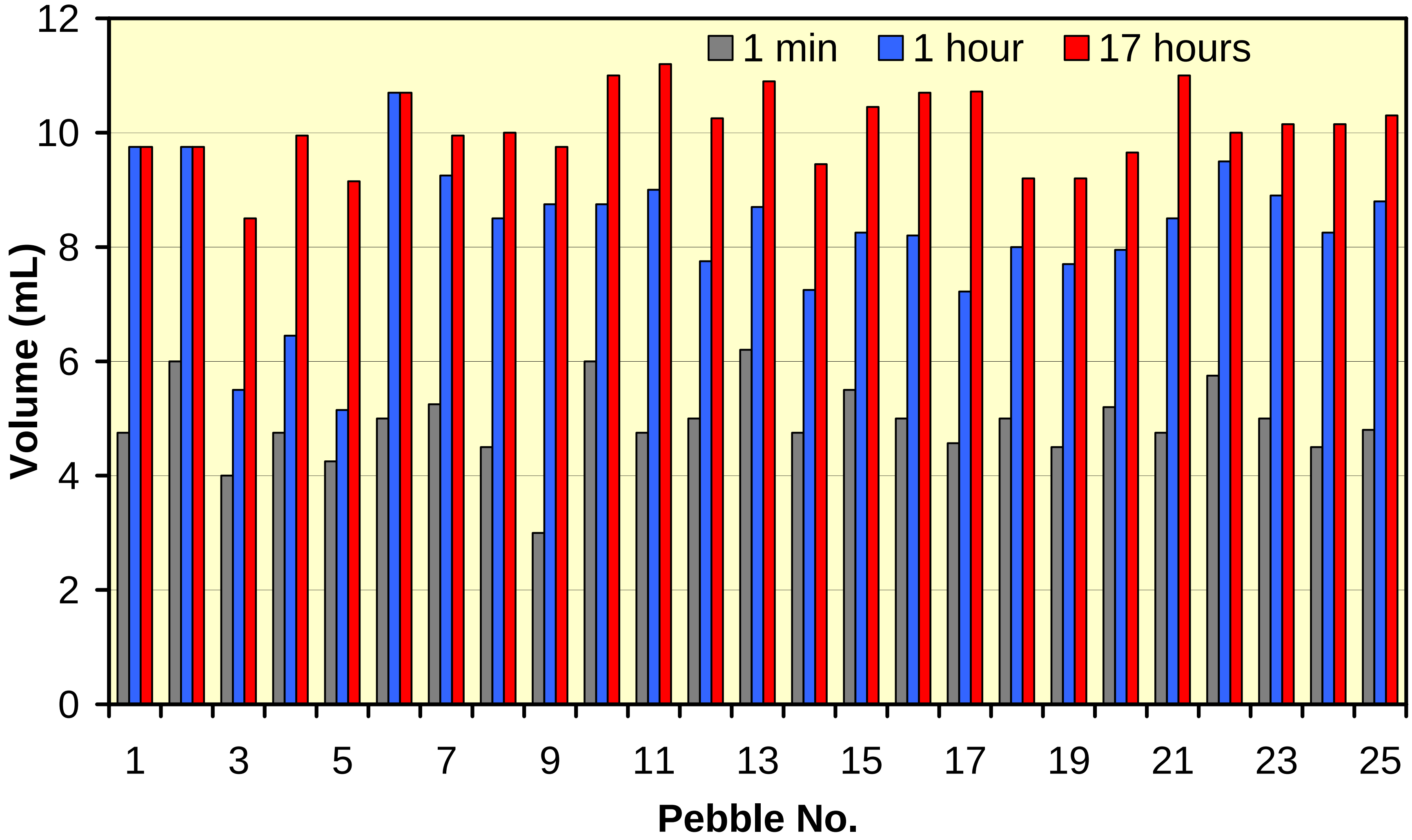

Figure 12: Take-up of water in cleaned graphite pebbles at 400 mbar

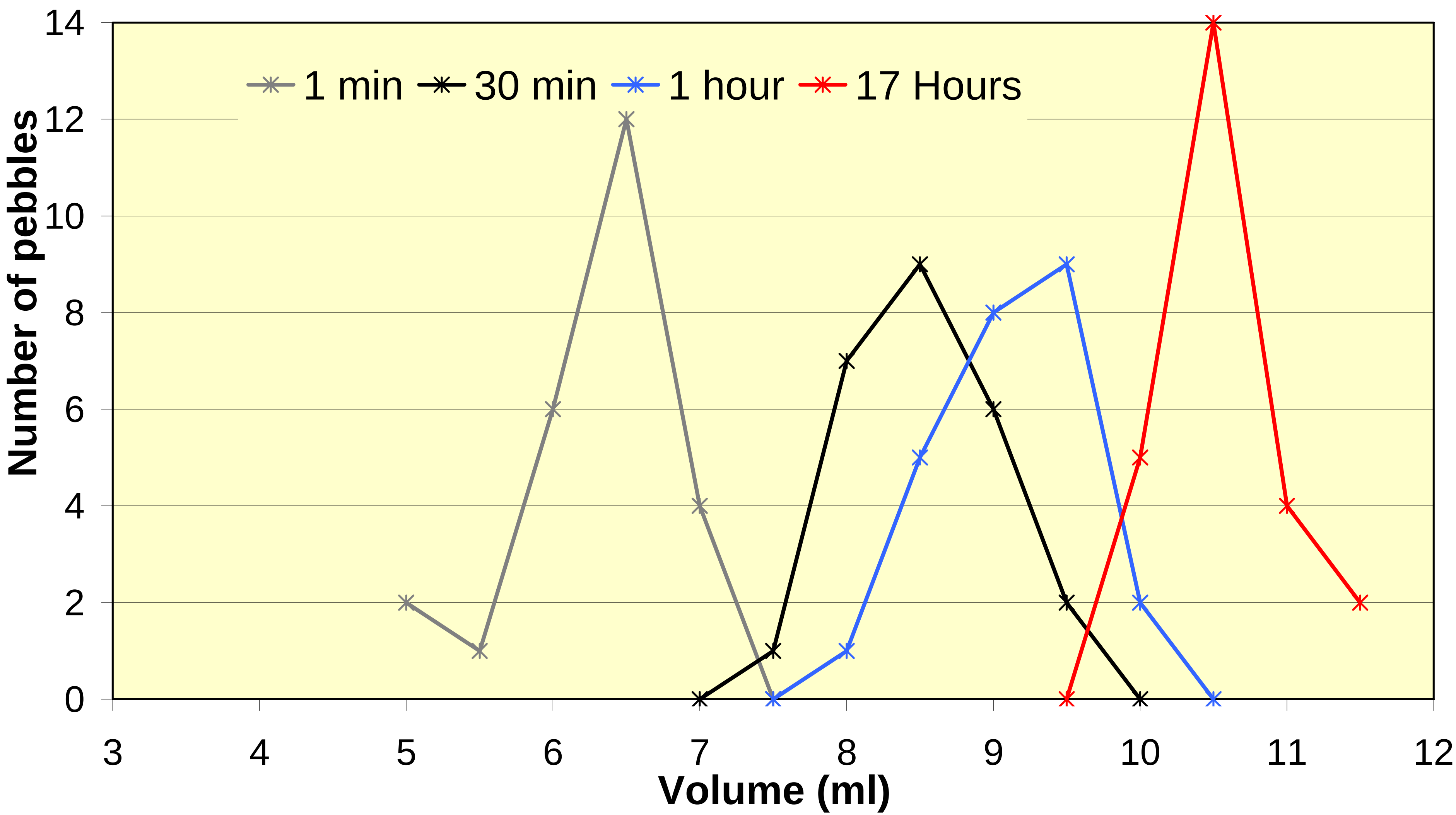

Figure 13: Distribution of the water take-up in cleaned pebbles at 400 mbar

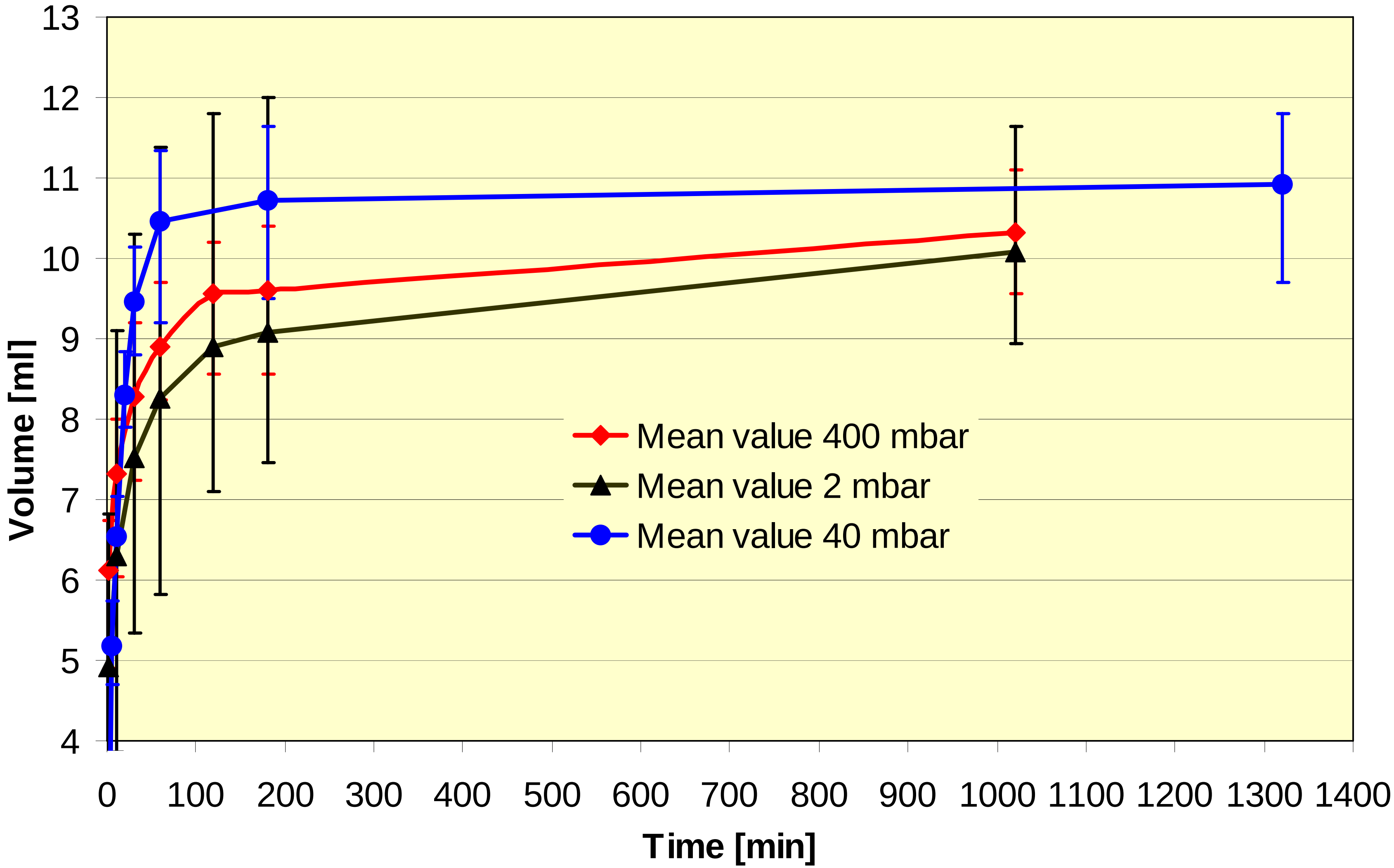

Figure 14: Comparison of the water take-up at different pressures

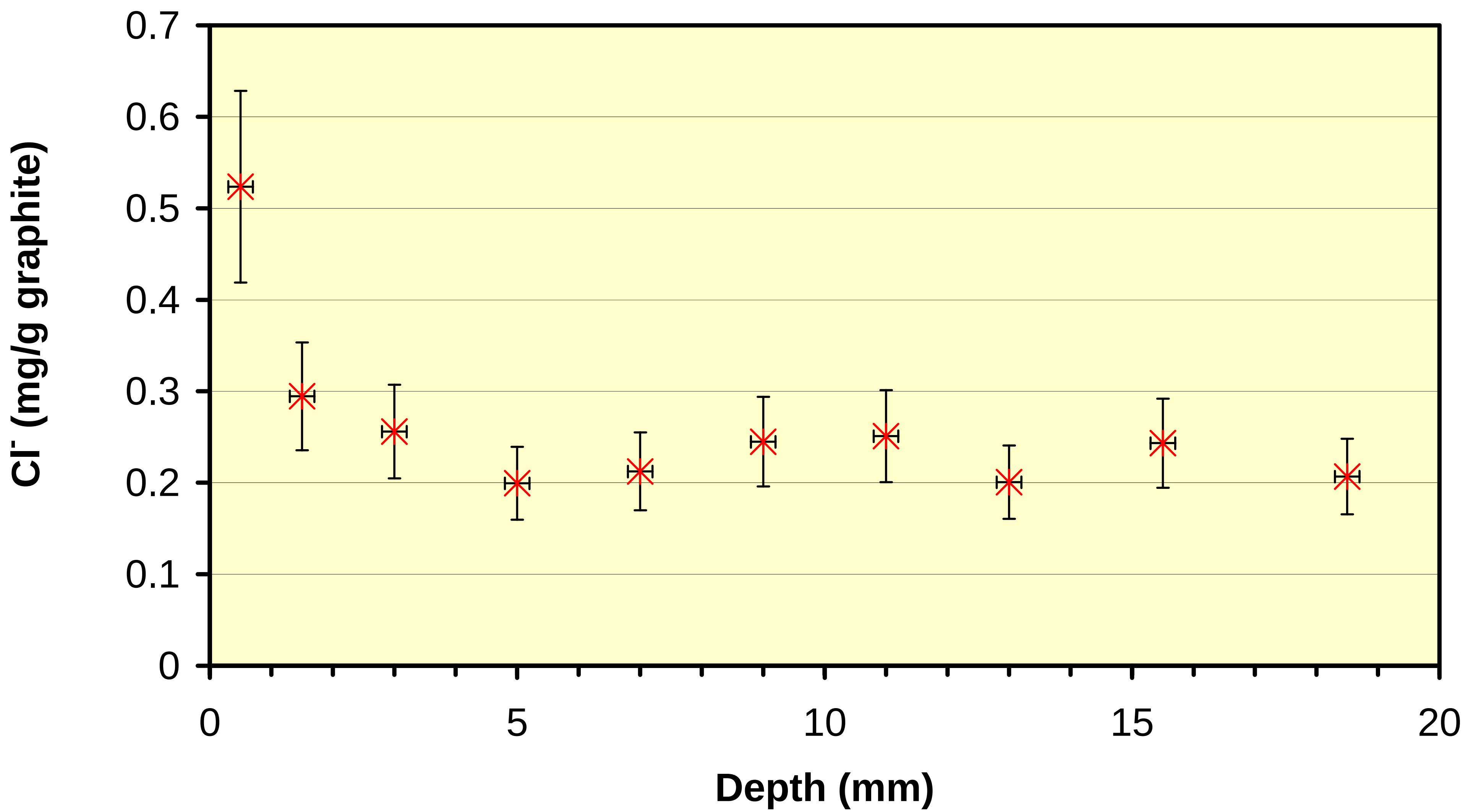

Figure 15: Chloride distribution in a pebble after saturation with 0.1 M NaCl solution

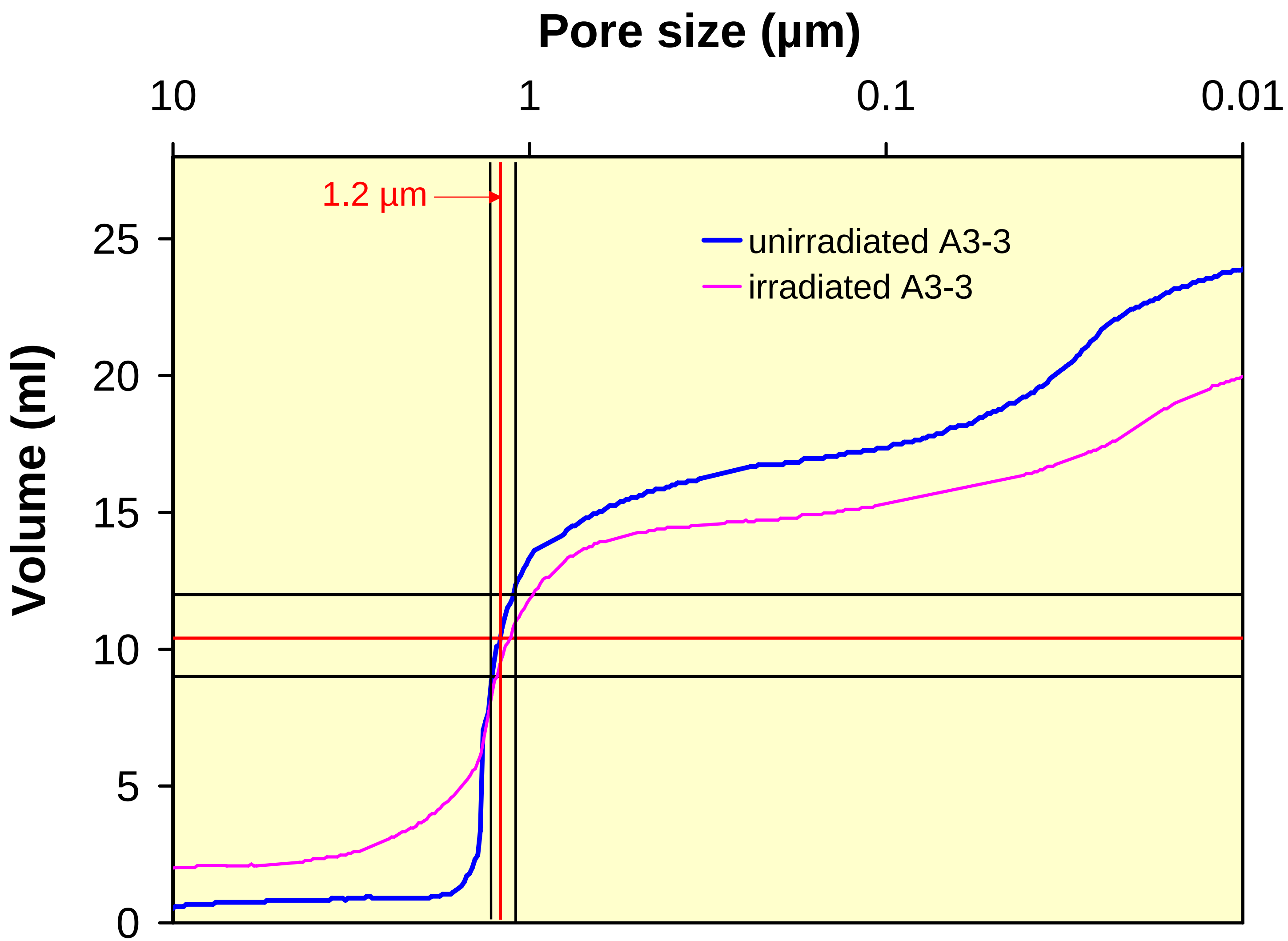

Figure 16: Pore size to volume correlation