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Study of the stability of Charpy V-notch reference test pieces for tests at 20 °C (ERM®-FA013ba, ERM®-FA015v and ERM®-FA016ax) during long-term storage at 18°C

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Abstract

In the frame of the certification of the Master Batches ERM®-FA013ba, ERM® FA015v and ERM®-FA016ax a long-term isochronous stability study was planned covering a storage period of 48 months with storage periods of 12, 24, 36 and 48 months at a storage temperature of 18 °C and using a reference temperature of -20 °C.
The results of the stability study indicate that the absolute values obtained for the different Master Batches agree within the respective uncertainties with the certified values as well as with values obtained during the certification of Secondary Batches and that there is no indication of instability of the Charpy Master Batches for a period of at least 10 years.
Moreover as the measurement uncertainty is the main contribution to the uncertainty of the certified value it is decided not to add an uncertainty contribution for stability to the certified uncertainty of the Master Batches.

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Summary

In the frame of the certification of the Master Batches ERM®-FA013ba, ERM®-FA015v and ERM®-FA016ax a long-term isochronous stability study was planned covering a storage period of 48 months with storage periods of 12, 24, 36 and 48 months at a storage temperature of 18 °C and using a reference temperature of -20 °C.

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Moreover as the measurement uncertainty is the main contribution to the uncertainty of the certified value it is decided not to add an uncertainty contribution for stability to the certified uncertainty of the Master Batches.

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Glossary

CRM	Certified Reference Material
EC	European Commission
ERM®	European Reference Material
IMB	International Master Batch
IRMM	Institute for Reference Materials and Measurements
ISO	International Organization for Standardization
JRC	Joint Research Centre
KV	Absorbed energy = energy required to break a V-notched test piece of defined shape and dimensions when tested with a pendulum impact testing machine
KV_{CRM}	Certified *KV* value of a set of 5 reference test pieces from the Secondary Batch
KV_{MB}	Certified *KV* value of the Master Batch test pieces
$KV_{18\ °\mathrm{C}}$	*KV* value of test pieces stored at 18 °C during the isochronous study
$KV_{-20\ °\mathrm{C}}$	*KV* value for test pieces stored at -20 °C during the isochronous study
MB	Master Batch
R	Ratio of *KV* values obtained at different storage temperatures
RSD	Relative standard deviation
SD	Standard deviation
SB	Secondary Batch
SE	Standard error
U	Expanded uncertainty (*k* = 2, confidence level of about 95 %)
u_{lts}	Standard uncertainty of the long-term stability
u_{ratio}	Standard uncertainty of the ratio of *KV* values obtained at different storage temperatures

1 Introduction

IRMM is one of the producers of certified reference materials (CRMs) for the Charpy pendulum impact test. The Charpy CRMs produced by IRMM are V-notched steel test pieces, and have a certified absorbed energy (*KV*) value. The main factor affecting the long-term stability of the certified *KV* value of these CRMs is storage temperature.

The long-term stability of the certified *KV* values was first systematically investigated for steel samples with a nominal *KV* value of 120 J by Pauwels *et al*. They tested Charpy samples that were stored at room temperature (around 18°C), and did not observe measurable changes of absorbed energy during a stability study of 3 years [1]. Additional evidence for the long-term stability of the reference test pieces produced from AISI 4340 steel of lower energy levels (nominally 15 J, 30 J and 100 J) and stored at room temperature for at least 3 years, has been obtained during the International Master Batch (IMB) project [2]. In the IMB-project, the stability of the certified test pieces was judged from the change of the mean of means of the absorbed energy obtained on 7 reference pendulums over a three year period. None of the three regression slopes for the tested energy levels was statistically significant at the 0.05 level. Given the large sample-to-sample heterogeneity and the limited number of samples (5) in a CRM unit, the uncertainty contribution from instability was therefore considered to be insignificant in comparison to that of homogeneity.

The main reason for the microstructural stability of the certified reference test pieces when stored at room temperature is the annealing treatment to which the samples were subjected after the austenisation treatment. Annealing is a part of the steel-making process that is performed at temperatures where the equilibrium phases are the same as the (meta-)stable phases at ambient temperature (α-Fe and Fe_3C). The only driving force for instability during storage at room temperature stems from the difference in solubility of interstitial elements in the α-Fe matrix, between annealing and room temperatures. Relaxation of residual (micro-)stress by short-range diffusion or the additional formation or growth of precipitates during the shelf-life of the certified reference test pieces is expected to proceed but slowly.

Rather than neglecting the stability issue, efforts are spent to better establish the stability of the certified values of batches of Charpy CRMs. Therefore a long-term stability study was set-up in the frame of the certification of the Master Batches ERM®-FA013ba, ERM®-FA015v and ERM®-FA016ax. Awaiting the results of this study, it was decided to specify a limited shelf-life for storage at room temperature. A period of 10 years was chosen, counting from the date of the characterisation tests on the SB.

This report describes the results and conclusions drawn from the stability study tests on Master Batches ERM®-FA013ba, ERM®-FA015v and ERM®-FA016ax.

2 Details of the isochronous long-term stability study

2.1 Design of the isochronous study

In the frame of the certification of the Master Batches ERM®-FA013ba, ERM®-FA015v and ERM®-FA016ax a long-term isochronous stability study [3] was set up starting 18/03/2008. Of each batch samples were stored at 18 °C during 12, 24, 36 and 48 months. This temperature is chosen as it is the preferred temperature for long-term storage of the Charpy test pieces, both at IRMM and at the customers' premises. The reference temperature (a temperature at which it is assumed that the reference material is stable) was chosen to be -20 °C. The isochronous study is designed to reveal differences between *KV* values of samples stored at the desired storage temperature (room temperature or 18°C) and the reference temperature (-20°C).

2.2 Charpy pendulum impact tests

For each batch 3 sets (of 5 test pieces each) were tested per time point (0, 12, 24, 36 and 48 months) in a randomised way on 19/04/2012 (ERM-FA013ba), on 24/04/2012 (ERM-FA015v) and on 26/04/2012 (ERM-FA016ax). All pendulum impact tests were performed at 20°C (which is the test temperature for which the absorbed energy (*KV*) values are certified) under conditions of repeatability, using the Instron Wolpert PW 30 (serial number 7300 H1527) machine of IRMM, a Charpy impact pendulum yearly verified according to procedures described in ISO 148-2 [4]. The measured *KV* values were corrected for friction and windage losses.

2.3 Results

2.3.1 ERM-FA013ba

The results of the tests performed on 26/04/2012 are summarised in the RM Unit Report of Analysis 2420, April 27, 2012 [5]. Table 1 summarises in the sequence of the tests, the numbers of the different sets, and the corresponding storage time at 18 °C during the isochronous study.

Table 1: Sequence of tests

Set number	Storage time at 18 °C (months)
159	36
6	0*
156	24
248	48
93	12
32	48
223	12
127	0*
233	24
30	36
170	48
54	12
23	24
246	36
180	0*

* Reference samples stored at -20 °C

For some samples (listed in Table 2) a significant mark of post-fracture deformation was observed on one of the long edges of the notched face of the sample (see Table 2 in [6]). Systematically, this indent is accompanied by a broader, smeared-out deformation of the diagonally opposite long edge (on the face of the sample opposite the notch). This suggests that the samples, during a second strike onto the anvils, were briefly caught between an anvil and a part of the swinging pendulum. This is a known phenomenon (called jamming) and it induces erroneously high measured *KV* values. For this technical reason, i.e. the occurrence of post-fracture deformation on the sample, 8 data were eliminated from the analysis. All other data were accepted. An analysis of the normality of the distribution of remaining *KV* values did not indicate a skewed distribution towards higher or lower absorbed energy values.

The same parasitic energy absorbing phenomenon occurred also for some of the other FA013 batches which were prepared previously. Furthermore, the FA013ba batch was tested on 15 other pendulums during an interlaboratory comparison [6], revealing that post-fracture energy absorption occurs only for a minority of the pendulums involved (3 out of 15 pendulums). The jamming phenomenon does not occur at the higher energies (batches ERM-FA015v and ERM-FA016ax).

Table 2: Number of data eliminated from analysis for ERM-FA013ba

Set number	Number of data eliminated
93	1
223	1
30	1
23	1
246	2
180	2

The accepted data were evaluated using SoftCRM 2.0.10, a software program (http://www.eie.gr/iopc/softcrm/) customised according to the specifications of IRMM. The results are summarised in Table 3 and Figure 1.

Table 3: *KV* Results of tests for ERM-FA013ba

	0 months $KV_{-20\,°C}$	**12 months** $KV_{18\,°C}$	**24 months** $KV_{18\,°C}$	**36 months** $KV_{18\,°C}$	**48 months** $KV_{18\,°C}$
Average KV per time point (J)	28.76	28.21	28.31	28.36	28.61
SD (J)	1.14	0.83	0.66	0.76	0.54
RSD (%)	3.96	2.93	2.33	2.68	1.90
Average all data (J)	28.45				
SD (J)	0.79				
RSD (%)	2.78				
N	67				
Average of time point averages (J)	28.45				
SD (J)	0.23				
RSD (%)	0.80				
n	5				
Slope (J/month)	-0.001				
SE Slope (J/month)	0.006				

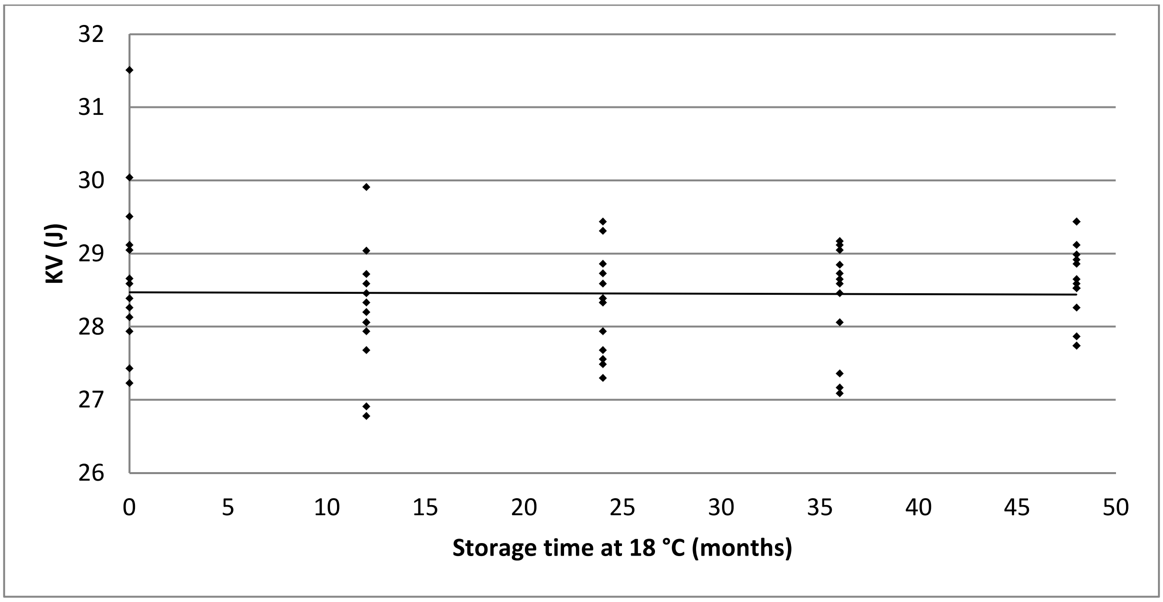

Figure 1: Graphical display of results obtained for ERM-FA013ba after storage of 0, 12, 24, 36 and 48 months at 18 °C

2.3.2 ERM-FA015v

The results of the tests performed on 19/04/2012 are summarised in the RM Unit Report of Analysis 2414, April 27, 2012 [7]. Table 4 summarises in the sequence of the tests the codes of the different sets (each comprising 5 test pieces) and the corresponding storage time at 18 °C. Results of the data evaluation with SoftCRM are summarised in Table 5 and Figure 2.

Table 4: Sequence of tests

Set number	Storage time at 18 °C (months)
51	12
176	0*
36	48
156	24
71	36
21	24
246	36
81	0*
251	48
183	12
174	48
92	12
193	24
111	36
4	0*

* Reference samples stored at -20 °C

Table 5: *KV* Results of tests for ERM-FA015v

	0 months $KV_{-20\ °C}$	**12 months** $KV_{18\ °C}$	**24 months** $KV_{18\ °C}$	**36 months** $KV_{18\ °C}$	**48 months** $KV_{18\ °C}$
Average per time point (J)	80.48	81.95	81.80	81.31	81.26
SD (J)	1.67	1.56	1.46	2.19	1.90
RSD (%)	2.07	1.90	1.79	2.70	2.33
Average all data (J)	81.36				
SD (J)	1.80				
RSD (%)	2.22				
n	75				
Average of time point averages (J)	81.36				
SD (J)	0.58				
RSD (%)	0.71				
n	5				
Slope (J/month)	0.008				
SE Slope (J/month)	0.012				

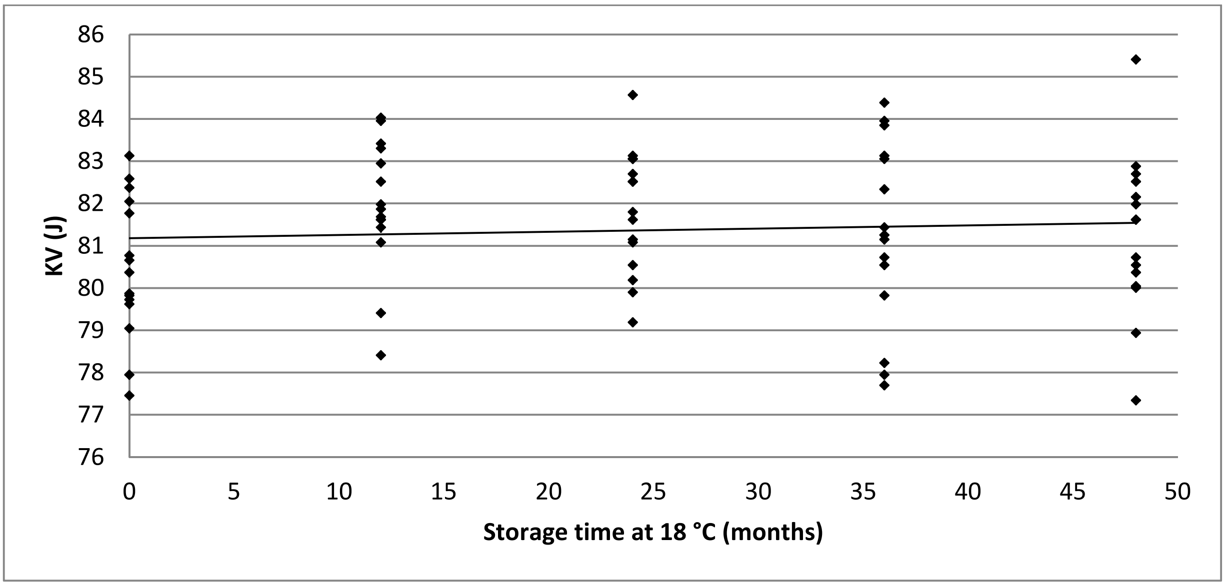

Figure 2: Graphical display of results obtained for ERM-FA015v after storage of 0, 12, 24, 36 and 48 months at 18 °C

2.3.3 ERM-FA016ax

The results of the tests performed on 24/04/2012 are summarised in the RM Unit Report of Analysis 2419, April 27, 2012 [8]. Table 6 summarises in the sequence of the tests the codes of the different sets (each comprising 5 test pieces) and the corresponding storage time at 18 °C. Results of the data evaluation with SoftCRM are summarised in Table 7 and Figure 3.

Table 6: Sequence of tests

Set number	Storage time at 18 °C (months)
96	12
161	36
32	48
217	0*
151	24
209	48
22	24
3	0*
201	36
52	12
133	0*
30	36
171	48
227	12
198	24

* Reference samples stored at -20 °C

Table 7: *KV* Results of tests for ERM-FA016ax

	0 months $KV_{-20\ °C}$	**12 months** $KV_{18\ °C}$	**24 months** $KV_{18\ °C}$	**36 months** $KV_{18\ °C}$	**48 months** $KV_{18\ °C}$
Average per time point (J)	128.50	127.85	127.82	127.08	128.32
SD (J)	3.55	3.39	3.37	3.74	3.63
RSD (%)	2.76	2.65	2.63	2.95	2.83
Average all data (J)	127.91				
SD (J)	3.48				
RSD (%)	2.72				
n	75				
Average of time point averages (J)	127.91				
SD (J)	0.55				
RSD (%)	0.43				
n	5				
Slope (J/month)	-0.009				
SE Slope (J/month)	0.024				

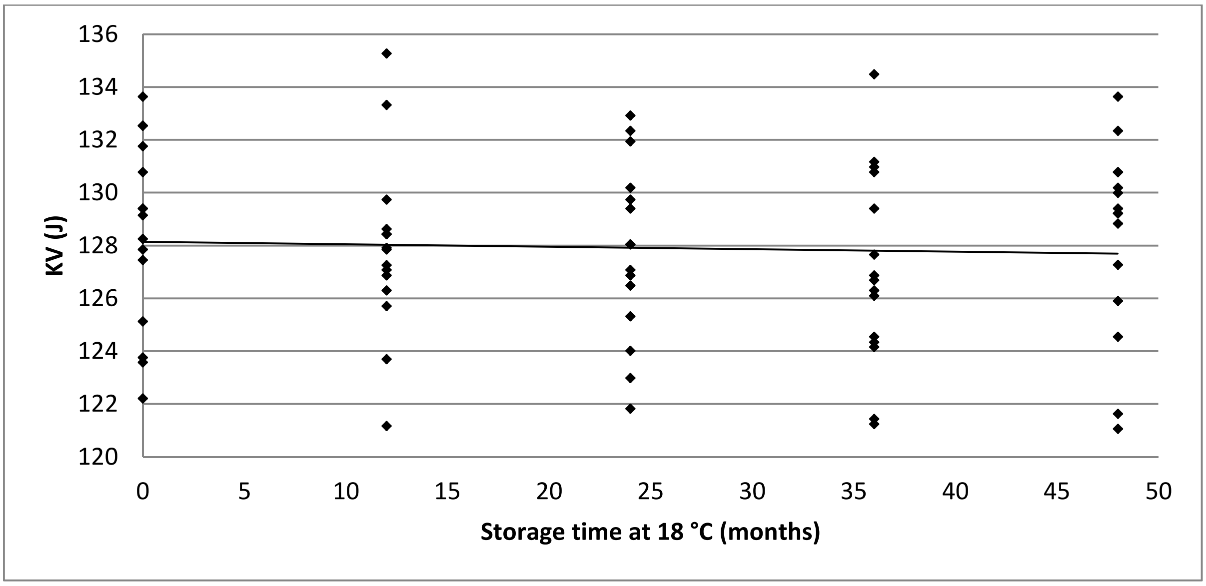

Figure 3: Graphical display of results obtained for ERM-FA016ax after storage of 0, 12, 24, 36 and 48 months at 18 °C

2.4 Evaluation of the results

Tables 3, 5 and 7 as well as Figures 1-3 indicate that the slope of the results is insignificant compared to the measurement precision of the *KV* measurements. As there are no significant differences between the results obtained after different periods of storage at 18 °C the data were pooled. The results (averages of all data) are summarised in Table 8.

Table 8: Summary of the averages (of all data) for the 3 Master Batches

	Average all data (J)	SD (J)	RSD (%)	n
FA013ba	28.45	0.79	2.78	67
FA015v	81.36	1.80	2.22	75
FA016ax	127.91	3.48	2.72	75

2.4.1 Comparison with certified values

The certified values are the result of three interlaboratory comparisons, one for each energy level, using a representative number of different types of pendulums (U-type and C-type, all with a 2 mm hammer) [6]. The resulting certified values are summarised in Table 9.

Table 9: Certified values of the Master Batches ERM-FA013ba, ERM-FA015v and ERM-FA016ax of Charpy V-notch reference test pieces

	Certified value KV_{MB} (J)	Standard uncertainty of KV_{MB} (J)	Relative standard uncertainty of KV_{MB} (%)	Number of pendulums
FA013ba	28.46	0.23	0.81	15
FA015v	81.32	0.51	0.63	16
FA016ax	126.82	0.93	0.73	14

Each Charpy impact pendulum gives slightly different values because the response of the pendulums is not calibrated. Instead, it is verified (at least yearly) whether the measured values obtained on reference materials are within the range allowed by ISO148-2 [4]. Consequently the values obtained on the IRMM pendulum cannot be directly compared to the certified values. Nevertheless, a comparison between the certified values from Table 9 and the measured values from Table 8 shows that the average values obtained during the stability study agree within the respective uncertainties with the certified values.

2.4.2 Comparison with previous measurements

The Master Batches have been used in the past in the frame of the certification of Secondary Batches for tests at 20°C. The results are summarised in Table 10 and Figure 4 (ERM-FA013ba), Table 11 and Figure 5 (ERM-FA015v) and Table 12 and Figure 6 (ERM-FA016ax).

Table 10: KV values obtained on Master Batch ERM-FA013ba during certification of Secondary Batches

Date	MB used in certification of	Value (J)	SD(J)	n
12/05/2008	FA013bc	28.02	0.9	23
24/11/2009	FA013bd	27.99	0.58	22
12/07/2010	FA013be	28.62	0.64	24
24/03/2010	FA013bf	28.23	0.88	23
19-20/10/2010	FA013bg/bh	28.15	0.83	38
16/02/2012	FA013bi	28.57	0.61	21
18/07/2012	FA013bj	28.89	0.9	24
17/08/2012	FA013bk	28.54	0.89	22
21/03/2013	FA013bl/bt	28.04	0.88	24
01/03/2013	FA013bs	27.61	1.01	25
01/08/2013	FA013bm	28.08	0.95	22
	Average	28.25	0.37*	

* SD of Average values

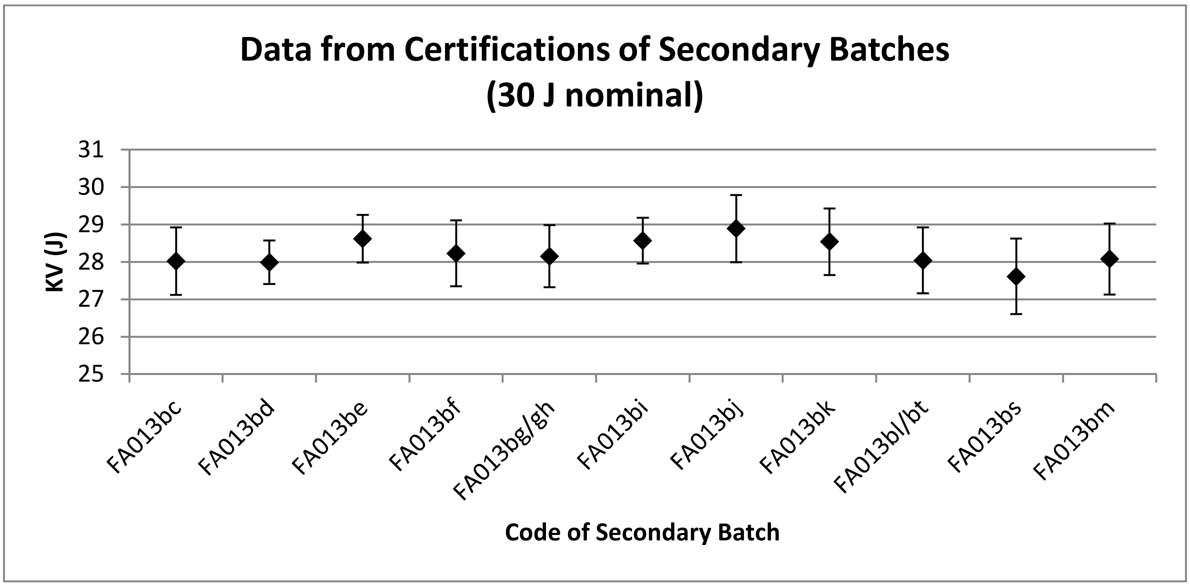

Figure 4: Graphical display of KV values obtained on Master Batch ERM-FA013ba during certification of Secondary Batches (error bars indicate SDs)

Table 11: KV values obtained on Master Batch ERM-FA015v during certification of Secondary Batches

Date	MB used in certification of	Value (J)	SD (J)	n
08/10/2009	FA015w	80.81	2.31	25
19-20/01/2011	FA015x/y	81.39	2.18	40

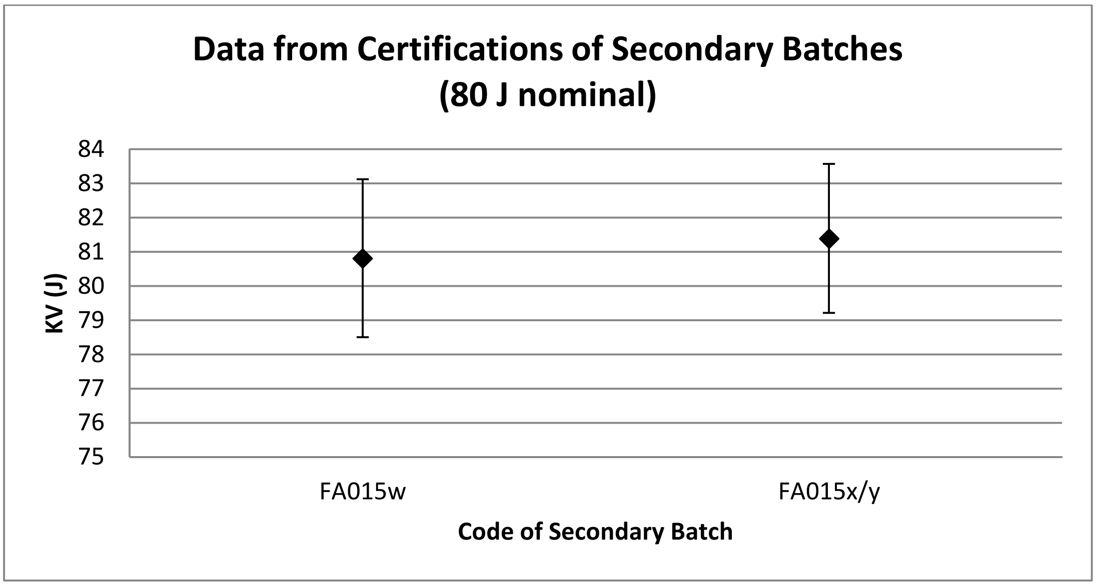

Figure 5: Graphical display of KV values obtained on Master Batch ERM-FA015v during certification of Secondary Batches (error bars indicate SDs)

Table 12: Values measured on Master Batch ERM-FA016ax during certification of Secondary Batches

Date	MB used in certification of	Value (J)	SD (J)	n
07/05/2009	FA016ba	127.55	3.68	25
23-24/08/2010	FA016bb/bc	130.83	3.53	40
13/09/2012	FA016be	128.87	1.93	25
06/12/2012	FA016bf	130.03	3.98	25
07/08/2013	FA016bg	128.17	3.58	25
	Average	129.09	1.34*	

* SD of Average values

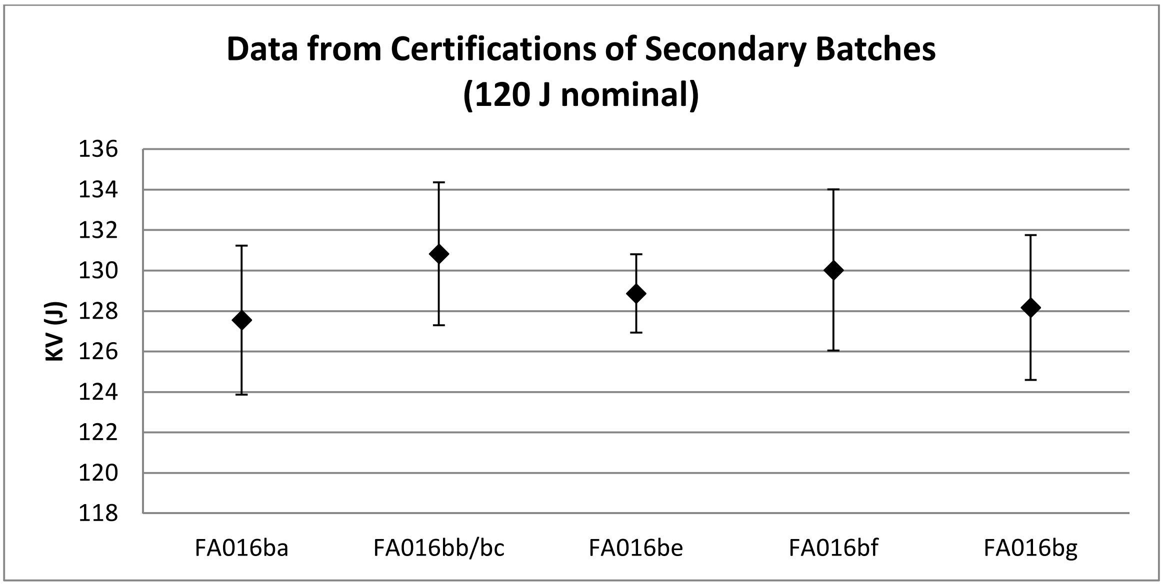

Figure 6: Graphical display of KV values obtained on Master Batch ERM-FA016ax during certification of Secondary Batches (error bars indicate SDs)

A comparison between the measured values from Table 8 and the values shown in Tables 10, 11 and 12 shows that the results of the stability study agree within the respective uncertainties with the average of the values obtained during the periodic certification of new Secondary Batches.

2.4.3 Comparison of ratios

The KV values obtained on the reference samples stored at -20 °C ($KV_{-20°C}$) can be compared to the KV values obtained on samples stored for different periods at 18 °C ($KV_{18°C}$). The ratio $R = KV_{18°C}/KV_{-20°C}$ indicates whether there is a degradation of the material during long-term storage as compared to the reference temperature. For the calculation of the uncertainties associated with this ratio, the respective uncertainty contributions of $KV_{18°C}$ and $KV_{-20°C}$ are taken into account; the uncertainties used only consist of the precision contributions to uncertainty, because the tests were done in repeatability conditions.

$$u_{ratio} = \sqrt{u_{KV18°C}^2 + u_{KV-20°C}^2}$$

The results are summarised in Table 13, which shows that all ratios cover unity within the respective uncertainties (u_{ratio}).

Table 13: Ratios $R = KV_{18°C}/KV_{-20°C}$ for the 3 Master Batches

	Ratio 0 month	u_{ratio}	Ratio 12 months	u_{ratio}	Ratio 24 months	u_{ratio}	Ratio 36 months	u_{ratio}	Ratio 48 months	u_{ratio}
FA013ba	1	0.056	0.981	0.048	0.984	0.045	0.986	0.047	0.995	0.044
FA015v	1	0.029	1.018	0.029	1.016	0.028	1.01	0.034	1.01	0.032
FA016ax	1	0.039	0.995	0.038	0.995	0.038	0.989	0.04	0.999	0.039

The uncertainty of the results of storage time 0 months reflects the measurement precision. The uncertainties obtained for storage times 12, 24, 36 and 48 months are of the same order of magnitude and also of the same order of magnitude as the value obtained for storage time 0. This indicates that the uncertainties reflect the measurement precision and provides further evidence that the materials are stable.

2.4.4 Calculation of long-term stability uncertainty contribution

A long-term stability contribution can be calculated using SoftCRM (Table 14), which applies the approach described in [3]. As the Master Batches have a long lifetime the contribution is calculated for a period of 10 years.

Table 14: Long-term uncertainty contribution u_{lts} (120 months)

	u_{lts} (120 months) (J)	u_{lts} (120 months) (%)
FA013ba	0.676	2.4
FA015v	1.473	1.8
FA016ax	2.838	2.2

In these calculations no corrections for measurement precision are made. The results suggest that the measurement precision practically accounts for the full long-term stability uncertainty contribution.

3 Conclusion

The results of the extensive long term isochronous stability study indicate that the absolute values obtained for the different Master Batches agree within the respective uncertainties with the certified values as well as with values obtained during the certification of Secondary Batches. No significant trend can be detected with storage time. There is no indication for instability of the Charpy Master Batches.

Moreover, as the measurement uncertainty is the main uncertainty contribution it is decided not to add an uncertainty contribution for stability to the certified uncertainty of the Master Batches.

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