

Relationship between Several Crushing Methods and Physical Concentration Behavior of Minor Rare Metals in Recycling of End-of-life PCBs

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Background

Japan's Four Strategies for the Security of Minor Rare Metals

**Development of
overseas mines**

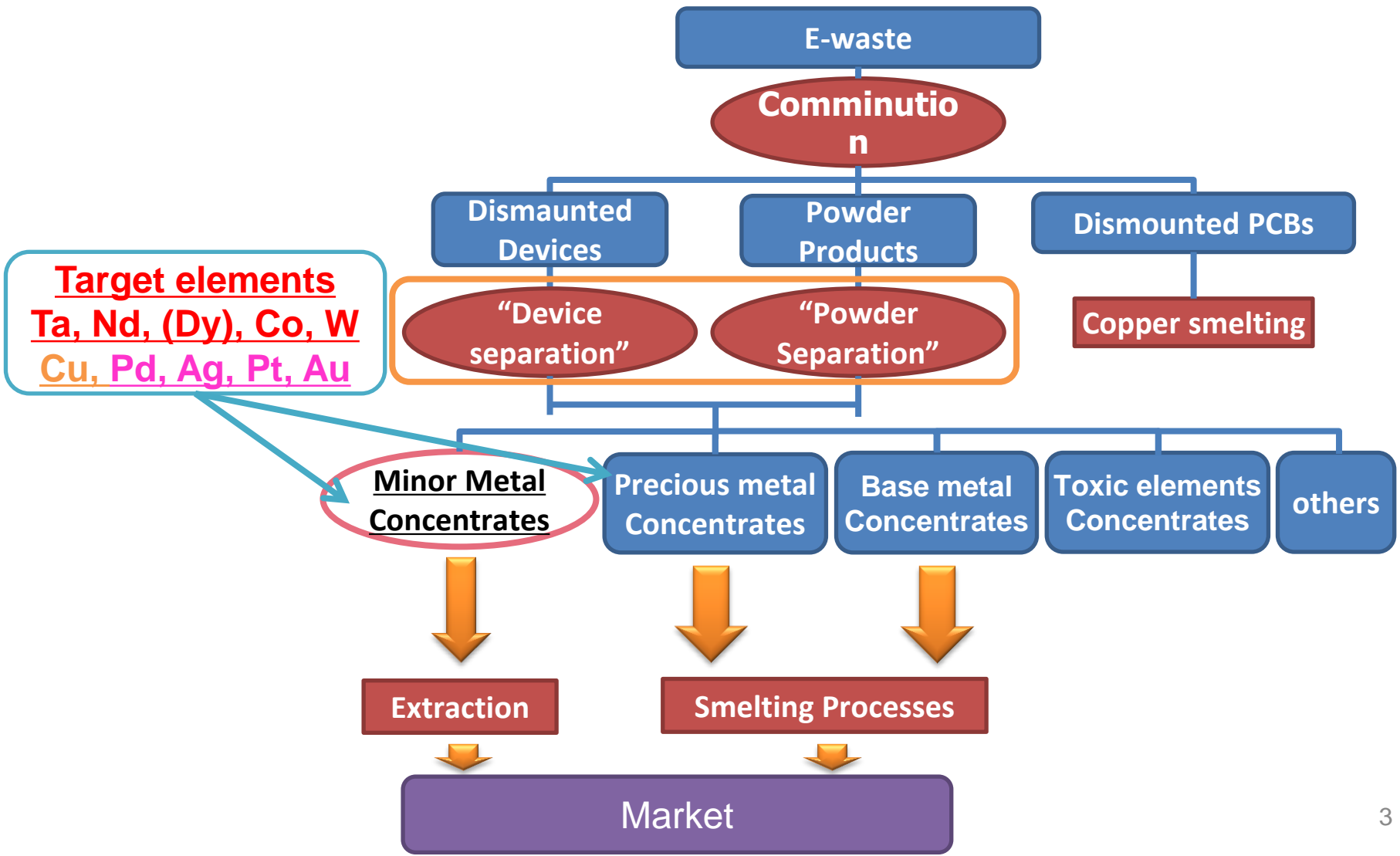
**Recycling of
e-wastes**
(Ta, Nd, Dy, Co, W)

**Finding out
replaceable elements**

**Increase domestic
stockpiles**
(V, Cr, Mn, Co, Ni, Mo, W, Ga, In)

Objective

Objective To concentrate minor rare metals from end-of-life electronics by combining unique comminutions and physical concentration methods.

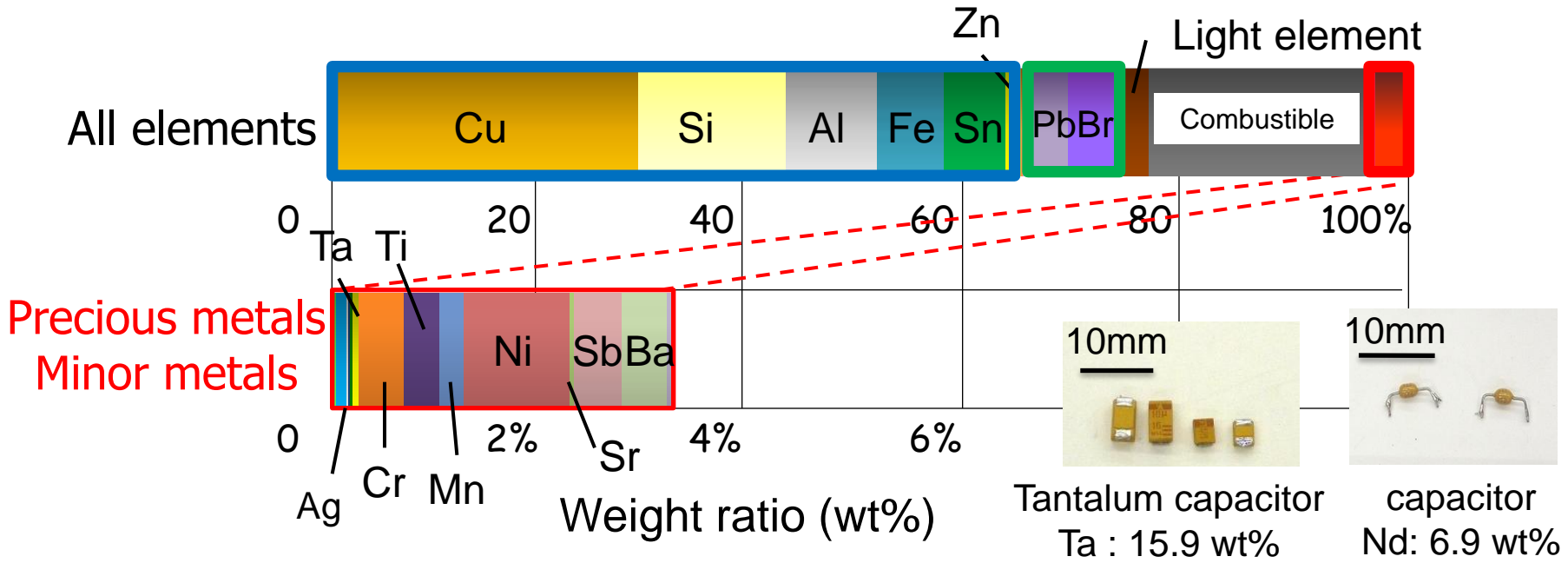


Experimental Sample



Sample PCBs

- PCB from Termination Device of digital subscriber line (Canada , 1996)
- Weight of PCBs 326g/piece
- Weight proportion of board to mantled devices 4 : 6

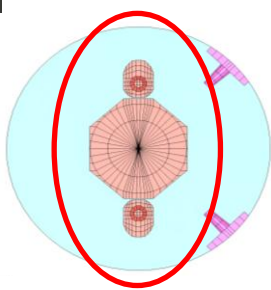


Mechanical Crushers Investigated (4 conditions)

Ball Mill (BM)

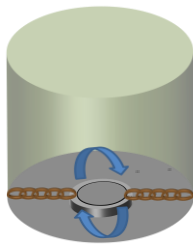


"Parts Separator (PS-1)"

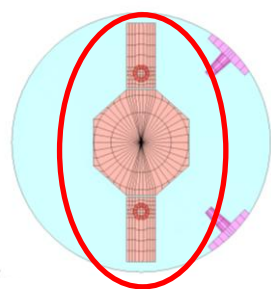


Short Blade

Cross Flow Shredder (CFS)



"Parts Separator" (PS-2)



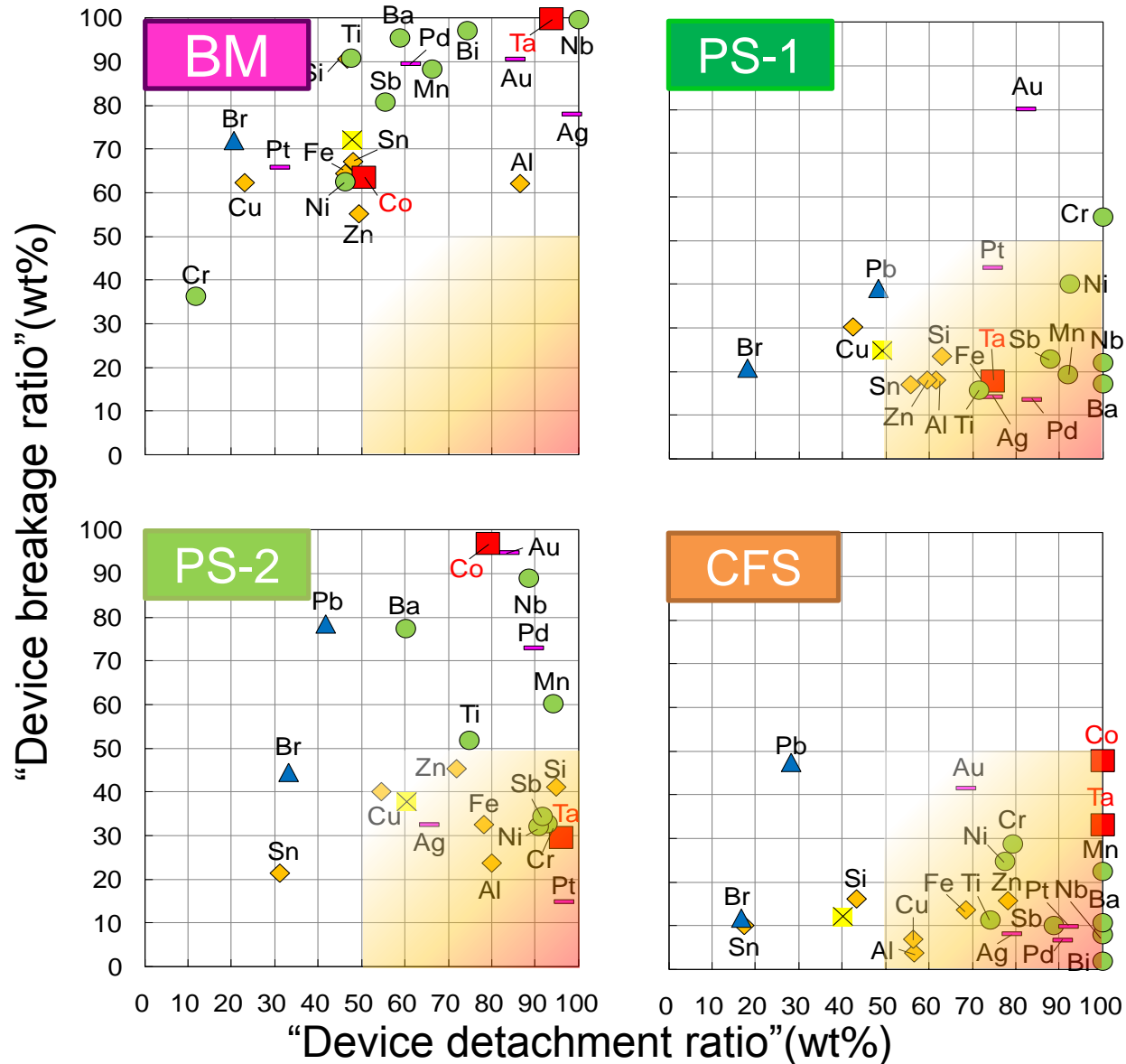
Long Blade

Table. Comminution Conditions

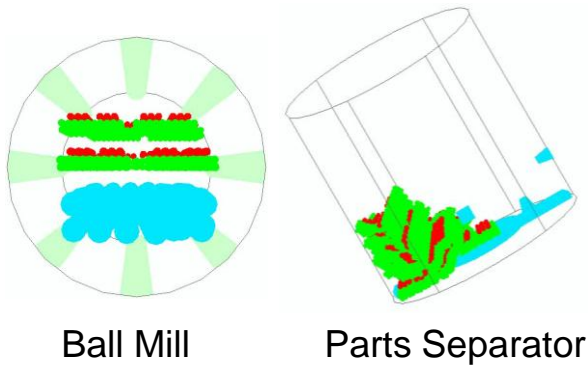
	PS-1	PS-2	CFS	BM
Rotation(rpm)	750	1000	700	42
Time (s)	120	90	5	2400

1. Comparison of each Crusher Product

Relationship between “Detachment ratio” and “Breakage ratio” of Devices



Comparison of Impact Energy Calculated from DEM



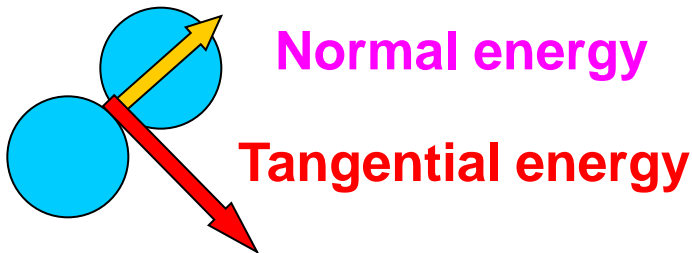
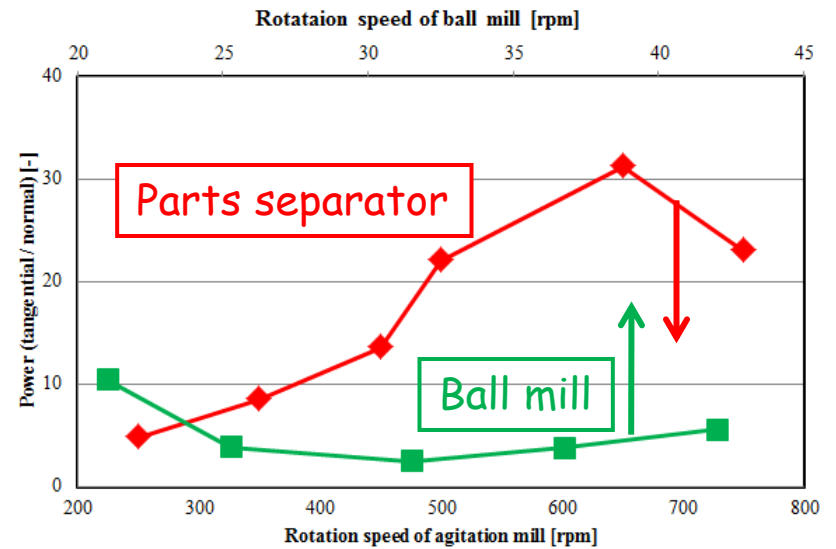
Ball Mill

Parts Separator

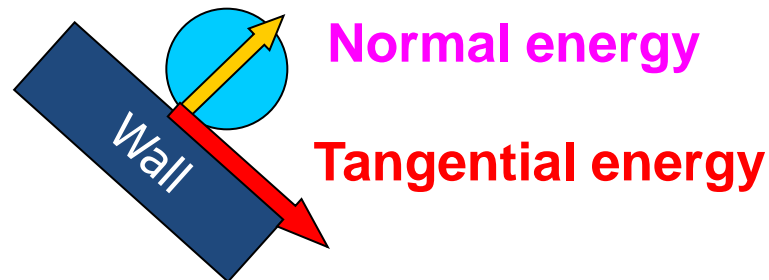
DEM Simulation
(DEM=Distinct Element Method)



Tangential / Normal energy ratio
vs Rotation speed



Normal energy
Tangential energy

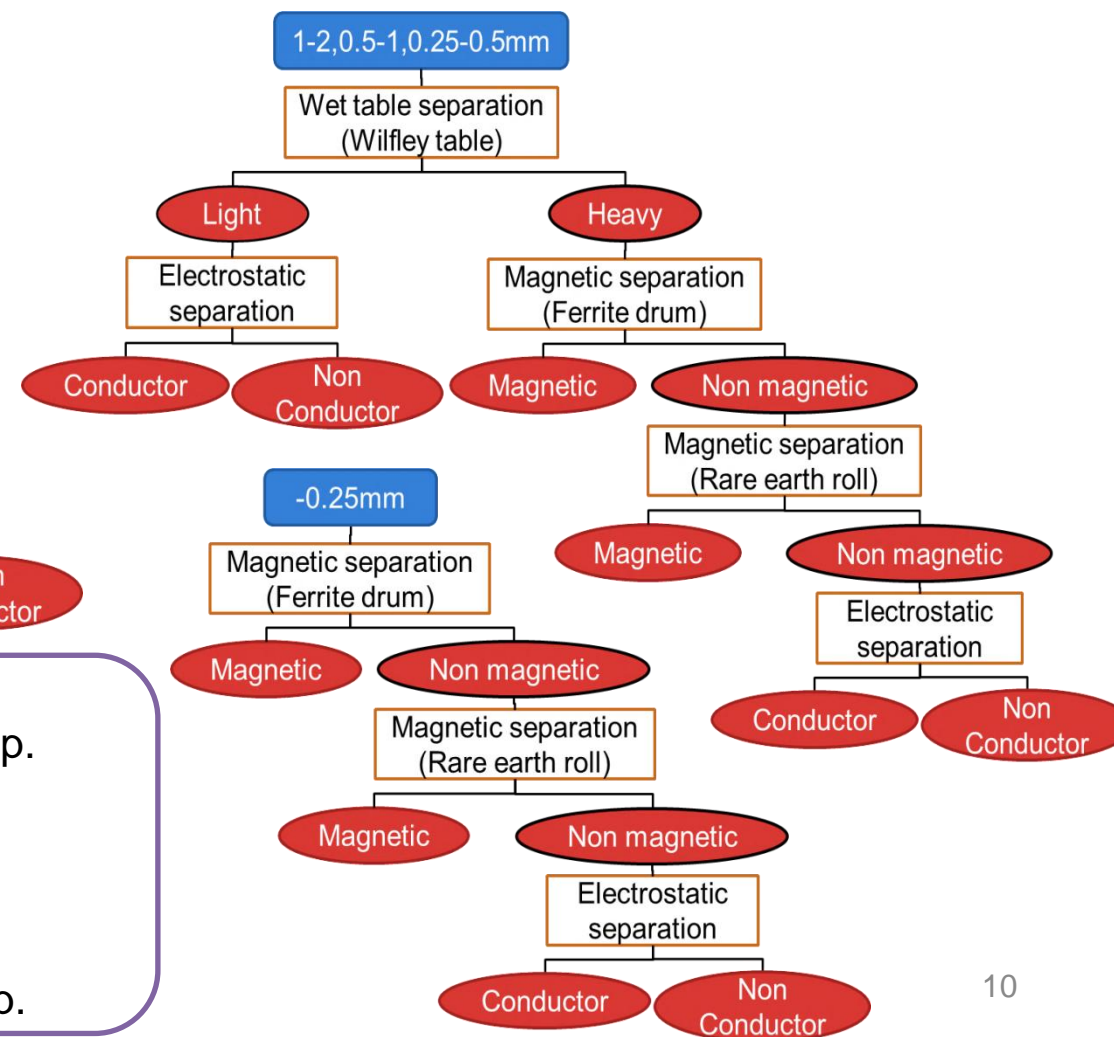
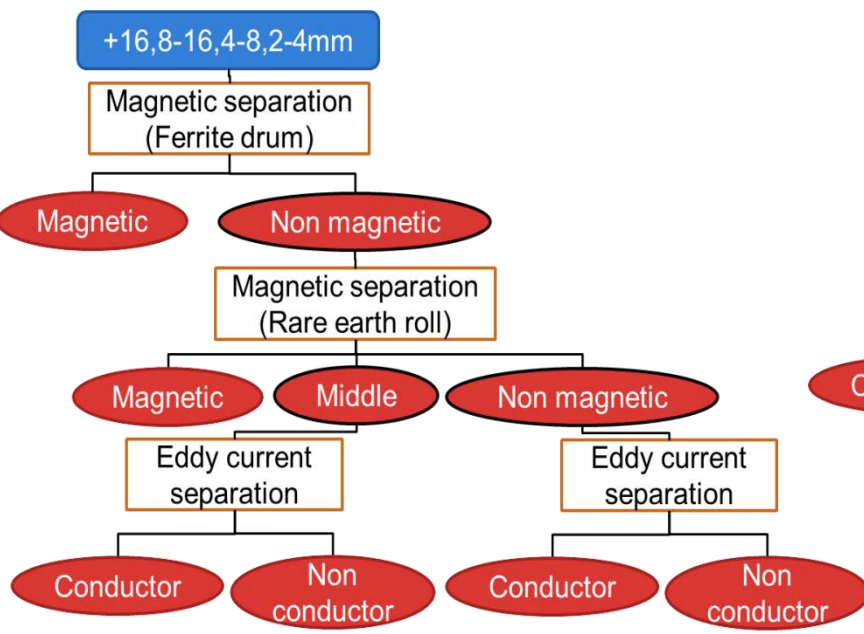


Normal energy
Tangential energy

2. Relationship between comminution method and separation behavior

Physical Separation Flow

2 types of physical separation flow were applied;
 "device separation" for dismantled electric devices from PCBs
 "powder separation" for detached particles (under 2 mm) from PCBs.

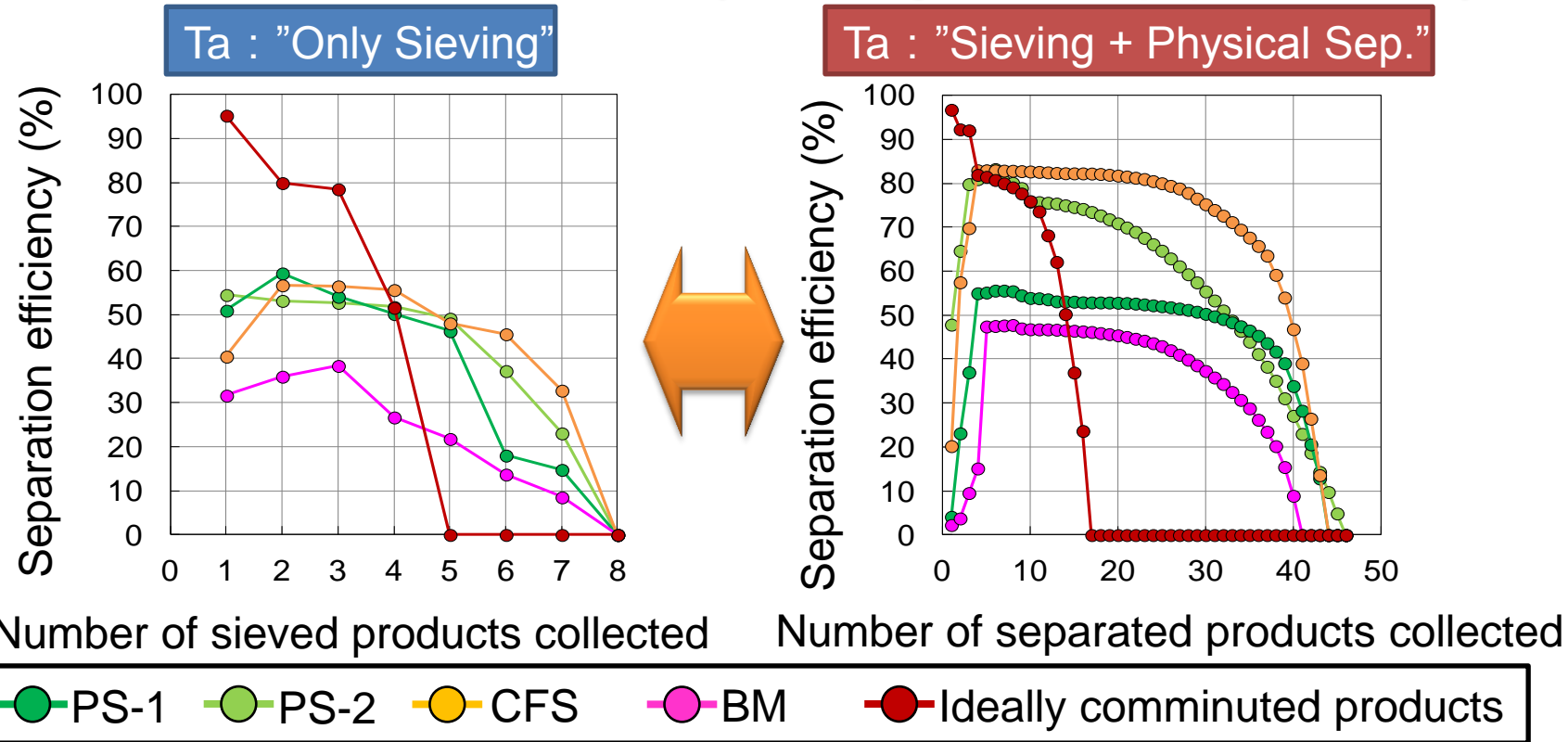


2-31.5mm
 2-step magnetic sep., Eddy current sep.

0.25-2mm
 Wet table sep., 2-step magnetic sep.,
 Electrostatic sep.

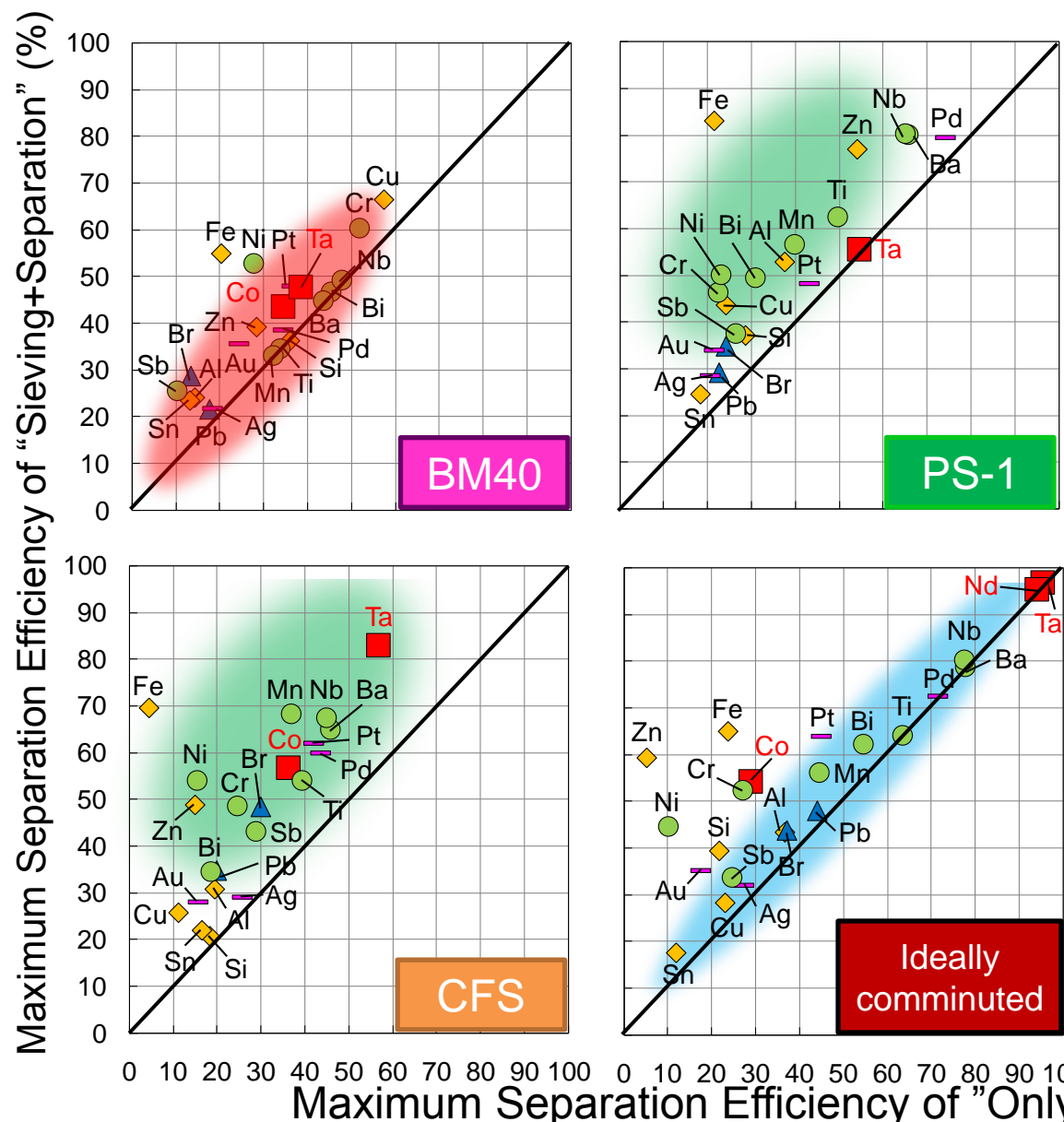
-0.25mm
 2-step magnetic sep., Electrostatic sep.

Influence of Comminution method on Separation Behavior (Analysis approach)

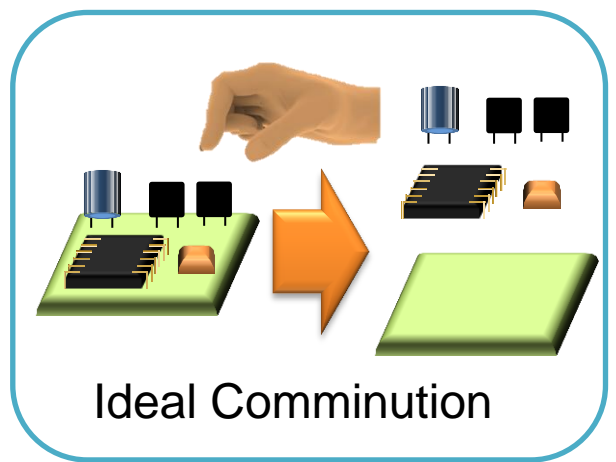


- (1) When collecting sieved products ("only sieving") or sieved and physically separated products ("Sieving + Physical Sep") in the order of each product grade, we calculated average grade, recovery rate and separation efficiency of these collected products.
- (2) From the result of (1), we show the relation between the number of collected products and separation efficiency.
- (3). Compare the maximum separation efficiency of "Only sieving" products to "Sieving+ Physical separation" products from the result of (2) for analysis of the influence of comminution.

Relationship between Max. Separation Efficiency of “Only sieving” and “Sieving+ Physical Separation”.



0 10 20 30 40 50 60 70 80 90 100



Ideal Comminution

Conclusion

- (1) When crushing condition is set properly, newly developed “Parts Separator” and ”Cross Flow Shredder” can detach electronic devices in non-destructive form from PCBs. This result suggests that shear force work effectively than compressive force for the detachment of devices.
- (2) Non-destructive device detachment from PCBs makes following physical concentration process more effective. Ideally detached devices can be concentrated only by sieving. However, for actual comminuted products, the combination of physical separation is effective for the concentration of minor rare metals.
- (3) In especial, for Minor metals that are contained in small number of device groups, non-destructive detachment is important to concentrate them physically.

Thank you for your attention!

Appendix

Device Detachment ratio · Breakage ratio

Optimal comminution condition for “Device separation”

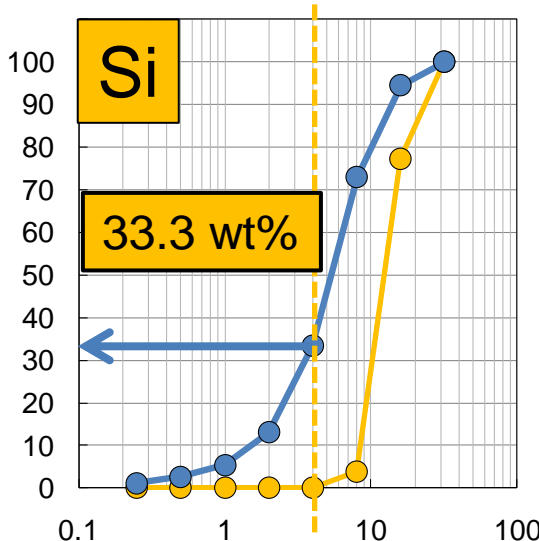
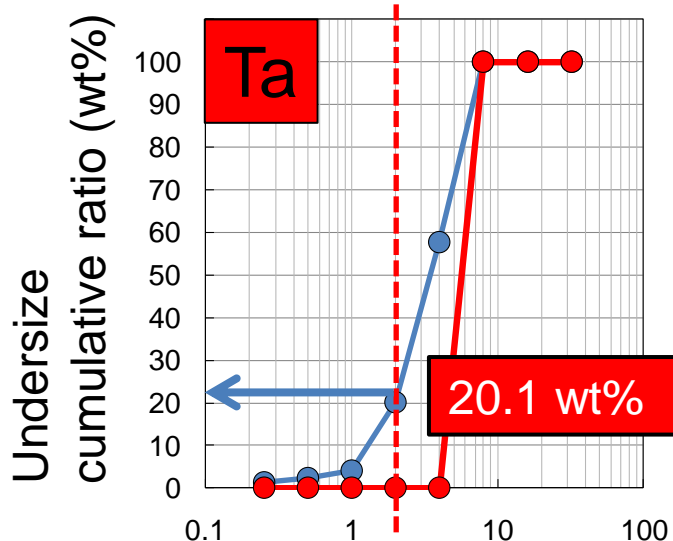
- ① Complete detachment from PCB
- ② Original shape of device remain

Definition of device detachment ratio

Ratio(wt%) of certain element weight in +31.5mm particle size fraction to whole feed amount of the element (PCBs remain over 31.5 mm)

Definition of device breakage ratio

Ratio(wt%) of certain element weight in particle size fraction under the minimum size of device that contain the element



Why these metals are set as Recycling target metals?

- These elements have high supply risk
(limited country has the natural deposit, price volatility)
- Price are relatively high.
- Amount of deposit from E-waste “Urban mine”

Crushers Comparison

Cross Flow Shredder (CFS)



- Conditions
- Rotation (rpm):700(800,600)
- Crushing Time (sec):5
- Sample Weight (kg):8.8



10cm Before



After Comminution



CFS Comminuted Products

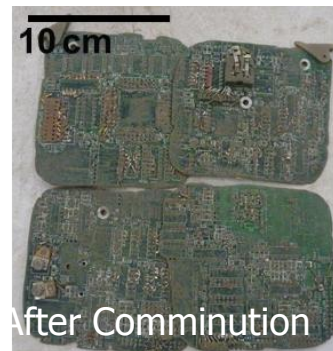
Ball Mill (BM40)



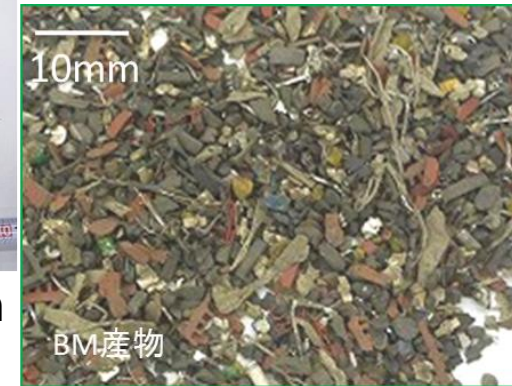
- Conditions
- Rotation(rpm):42
- Crushing time(sec):2400(40min)
- Weight(kg):4.8



Before comminution



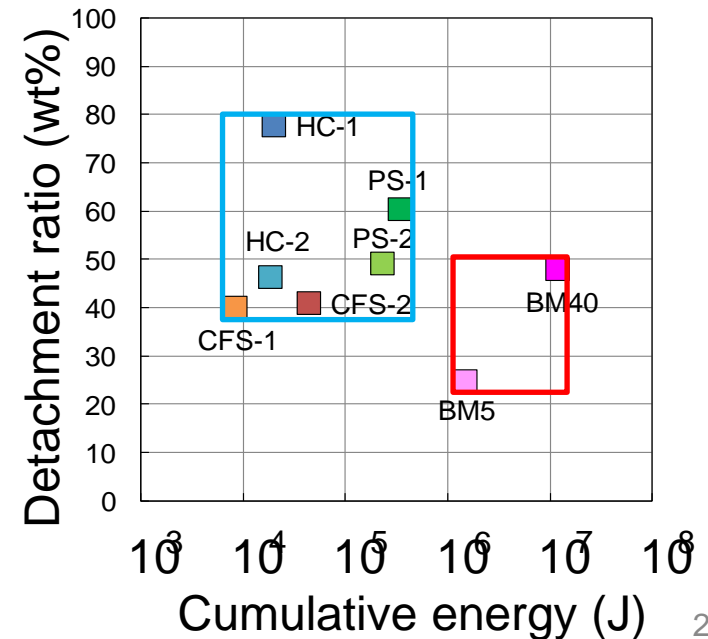
After Comminution



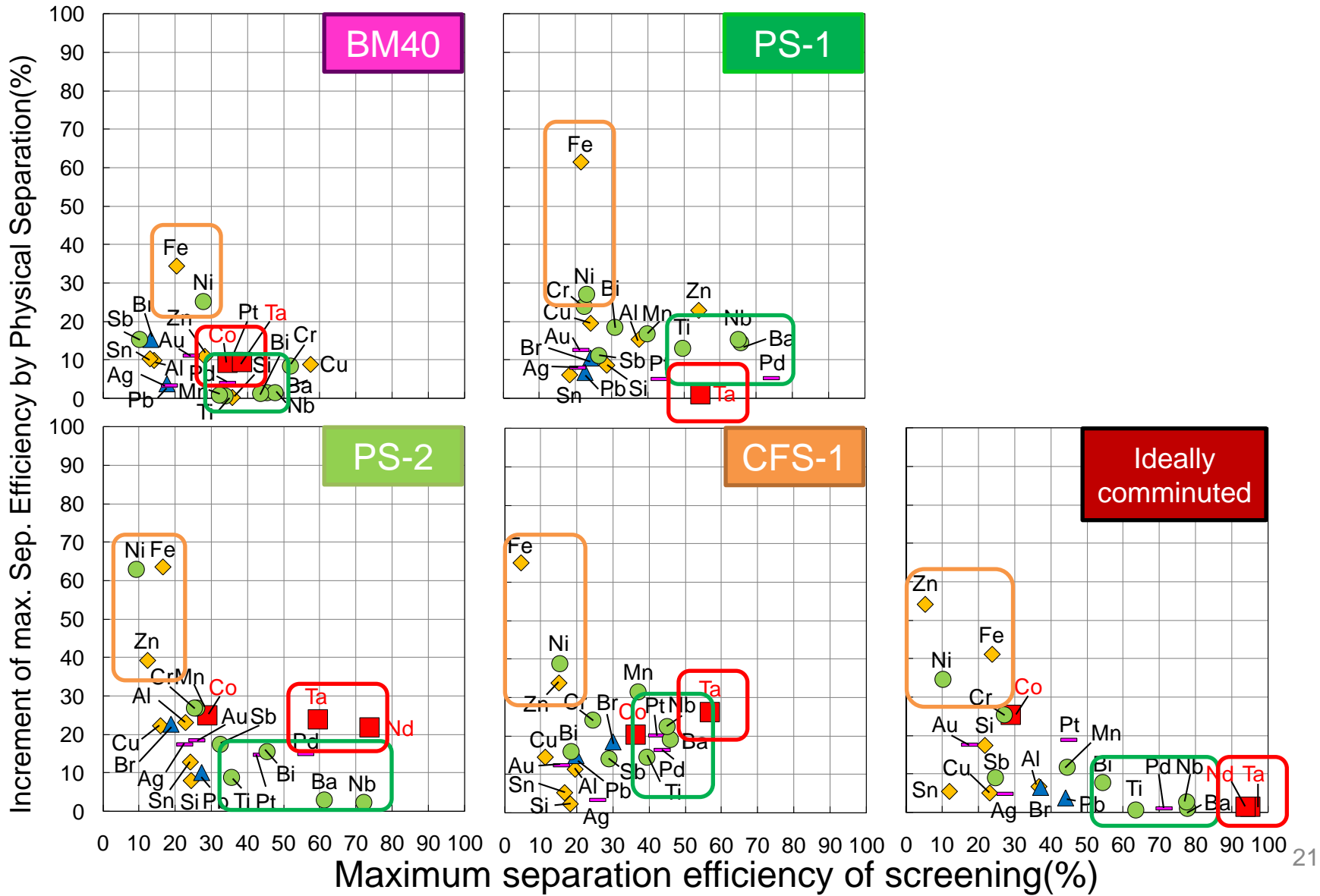
BM40 Comminuted products

About ball mill

- Ball Mill needs more time to detach devices
- Why not Larger Ball Mill ?
 - X Shortage of Sample PCBs
 - X more serious device breakage



Effect of Physical Separation for Each Element



Ta grade	Distribution ratio of Ta in this separated product from whole sample	Ta Weight (g)	Weight of separated product	Name of physically separated product
3.30	21.12	1.05	31.69681058	4-8mm RRMidNonCon
0.76	45.64	2.26	296.4308784	4-8mm FDMag
0.63	15.87	0.79	125.4370895	2-4mm FDMag
0.58	17.32	0.86	147.4318683	2-4mm RRMag
		0.00	0.317811951	2-4mm RRMidCon



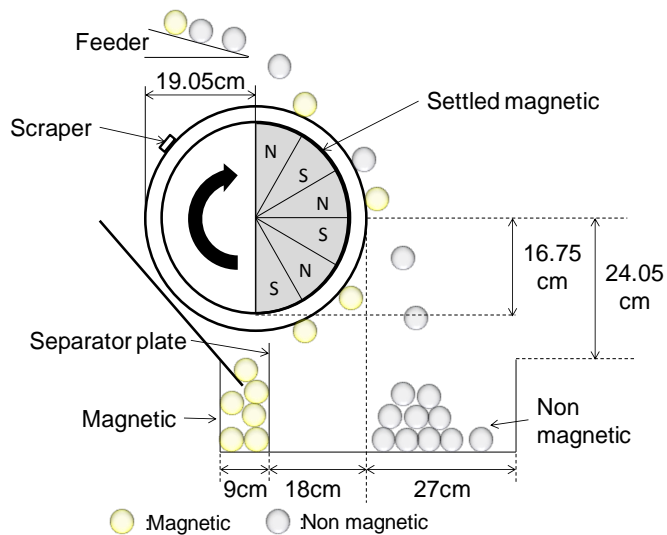
CFS



Separators



FD magnetic separator



RR magnetic separator

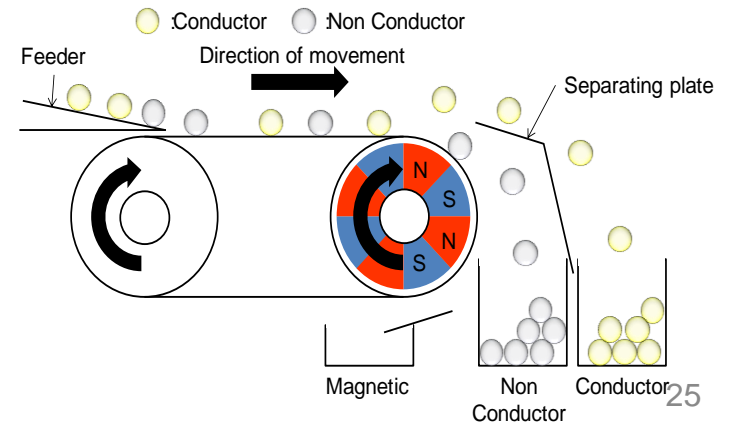
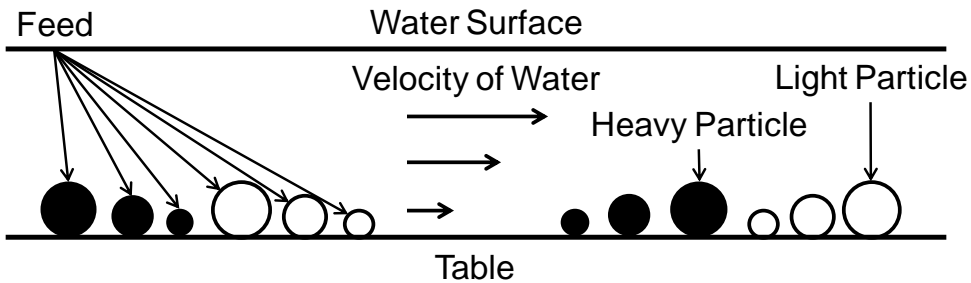
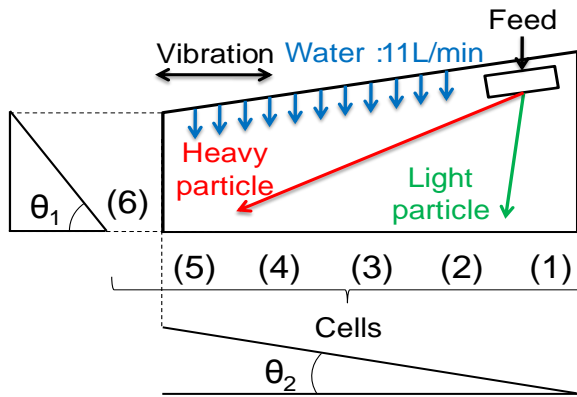
Separators



Wet table separator



Fig.6.5 Eddy current separator



Result of Physical Concentration (best condition)

Elements	Recovery (%)	Grade (wt.%)	Enrichment ratio	Grade of typical ore (wt.%)
Ta	97.7	3.32	32.4	0.24
W	97.4	10.01	27.3	0.58
Nd	67.2	1.66	9.5	0.64
Dy	100.0	0.31	14.6	0.002
Co	79.9	0.13	4.5	0.038
Cu	42.5	15.53	1.1	0.51
Ni	52.1	5.95	3.8	1.29
Au	62.3	0.05	1.6	0.00011
Ag	60.5	0.11	1.6	0.00248
Zn	20.0	5.22	0.8	1.09
Pb	6.0	6.24	9.6	5.84

These are the comparison of effect of physical separation for each crusher.

As mentioned at previous slide, some minor metal are concentrated more by physical separation.

As for precious metals and common metals, we can recognize that only low contribution can be made both by sieving and physical separation. Then, these elements should be eliminated from the minor rare metal concentrates and fed to non-ferrous metals smelting.

It is also observed that ferromagnetic iron and Nickel can be concentrated in any cases by physical separation especially by FD magnetic separation.

Other result differences among each elements probably stems from the difference of utilization range for various electronic devices.

こちらが両者の比較です。

これより「パーツセパレータ-1」「パーツセパレータ-2」「クロスフローシュレッダ-1」産物および「理想部品選別」では着目レアメタルである Ta, NdやNb, Ti, Pd等はそのプロットが相対的に右側に位置していることからふるい分けの寄与が大きいことが分かります。

一方, Au, Ag, Cu等の貴金属およびベースメタル類では「ボールミル」粉碎以外では, ふるい分け・物理選別の効果は同程度で低いことが分かります。また, いずれの粉碎条件でも強磁性体であるFe, Niは物理選別の寄与が大きかったことが分かります。

ここで, このような結果が表れた原因が各元素の特定部品への濃集状態の差にあると考えました。

重回帰分析による各元素の濃縮への影響の考察

各元素の濃縮するうえで何が影響しているのかを考察するため重回帰分析を行った

従属変数 : 各元素のフィードに対する「ふるい分け+物理選別」の最大分離効率を

達成した時の富鉱比

独立変数1 : フィード品位

独立変数2 : 部品破壊率

独立変数3 : 90%回収部品種類数

表.各粉砕条件における偏回帰係数

粉砕機	フィード品位	部品破壊率	90%回収部品種類数
PS-1	-0.046	-0.154	-0.635
PS-2	-0.067	0.250	-0.461
CFS-1	-0.179	-0.003	-0.586
BM40	-0.235	-0.677	-0.370
理想部品選別	-0.029	-0.176	-0.464

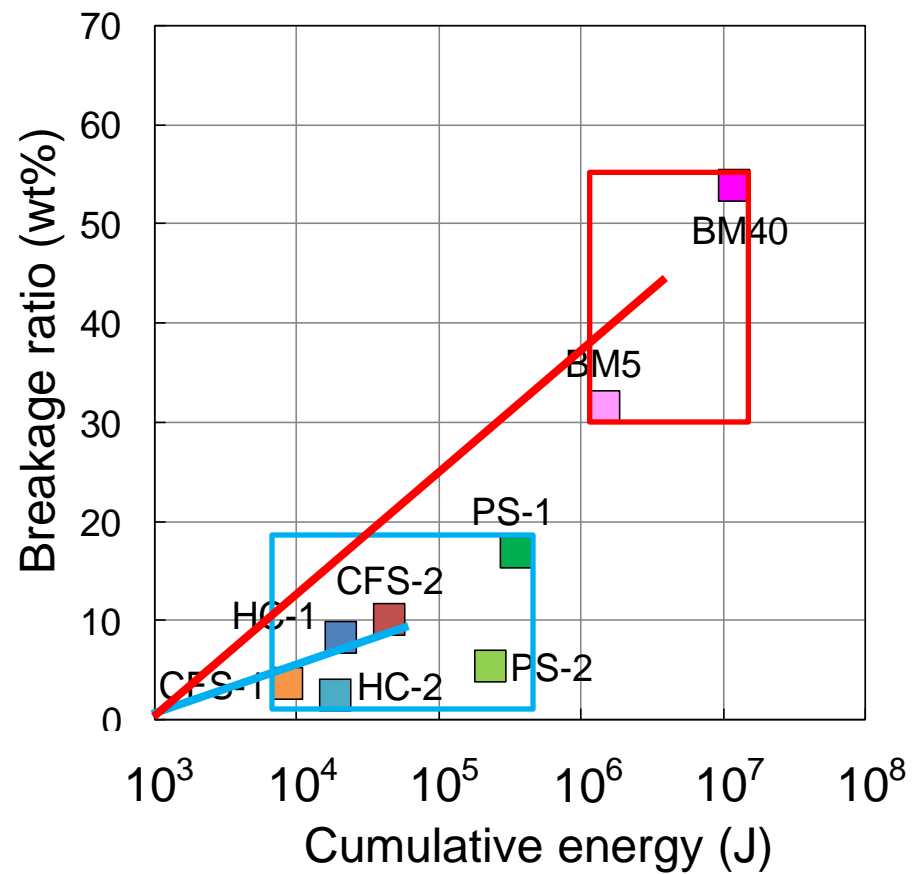
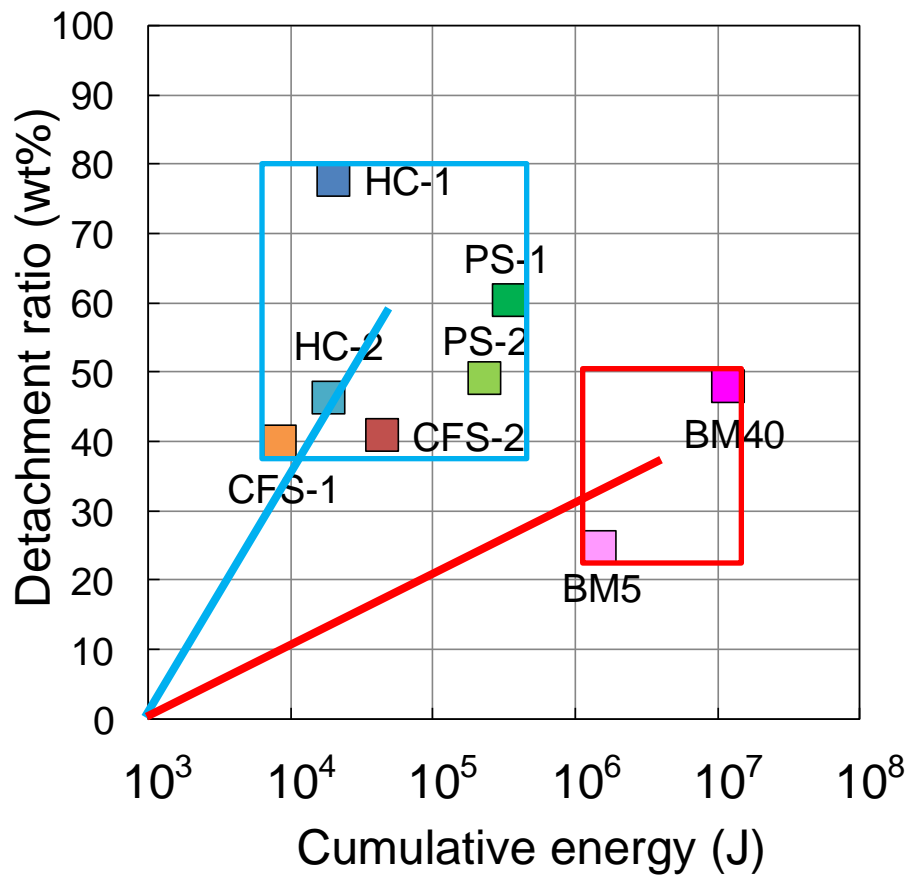
影響

・ ボールミルの結果より，過粉砕の状態になってしまうと濃縮挙動に悪影響を及ぼす

さらに，本研究における濃縮プロセスでどのような要因が濃縮挙動に影響したのかを調査するため，重回帰分析を行ないました。

従属変数としては各元素のフィードに対する「ふるい分け+物理選別」の最大分離効率を達成した時の富鉱比を設定しました。また，独立変数としてはフィード品位，部品破壊率，90%回収部品種類数の3つを用いました。

こちらの表に重回帰分析によって得られた偏回帰係数を示します。この結果より，いずれの粉碎条件においても90%回収部品種類数，すなわち各元素の部品への分散状態が濃縮に影響していることが分かります。また，ボールミル粉碎の結果より過粉碎も濃縮挙動に大きく影響を及ぼすことも分かりました。

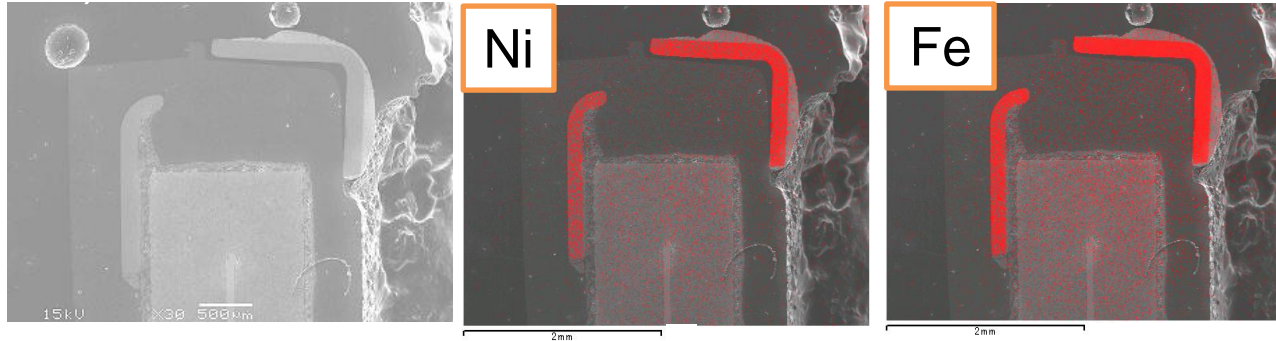


Cumulative Energy Consumption for “Device Detachment” and “Device Breakage”

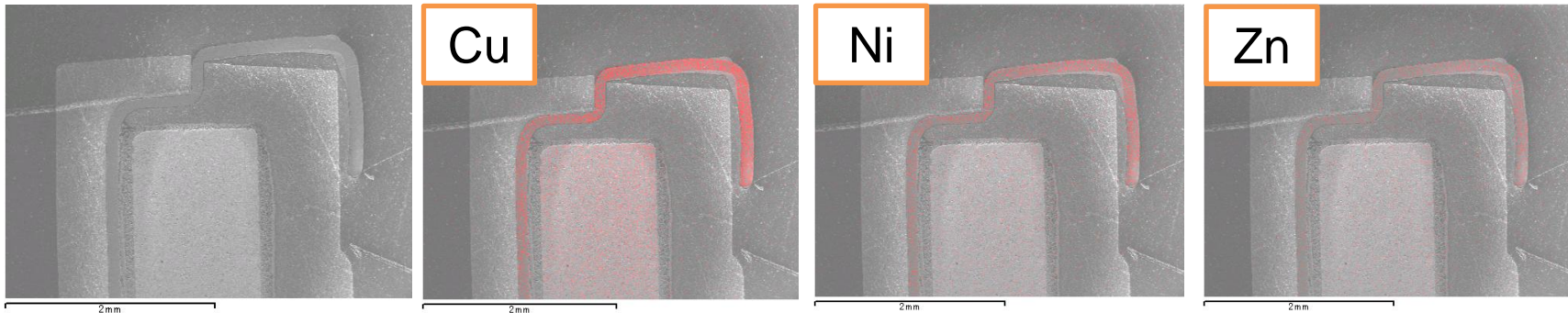
- Energy was consumed relatively for “Device Detachment” in PS, CFS, and HC, but for “Device Breakage” in BM.

タンタルコンデンサの構造(SEM-EDS分析)

磁着したTaコンデンサの電極(PS-2, CFS-1に存在)



磁着しなかったTaコンデンサの電極(PS-1に存在)



PS-1の粉碎産物には電極素材が強磁性体でないタンタルコンデンサが多く存在しており，それらがフェライトドラム磁選で回収されなかったため多産物に分散した

→レアメタルを多く使用する実装部品においては，部品を製造する段階で各種素材をある程度統一することが重要

背景・目的

レアメタルの問題点

- ・ 賦存量が少ないか，広く分布していても経済的に採掘可能な鉱床が少ない
- ・ 単体として抽出するのが技術的・経済的に困難
- ・ 地域偏在性が大きく，産出国は中国，南アフリカ，ロシアなどに集中

➔ レアメタル安定供給確保が重要となる

レアメタル確保戦略(経産省・環境省)

- ① 海外資源確保 (資源外交の戦略的取り組み・資源開発)
- ② リサイクリング (小型家電のリサイクルシステム構築)
- ③ 代替材料開発 (レアメタルの代替材料開発)
- ④ 国家備蓄

レアメタルリサイクリングの現状

現在ではFe,Cu,貴金属及び一部のレアメタルは回収・再利用がなされてきているが，製錬過程でCuより卑なる元素は酸化され，スラグ中に混入してしまい，それらの元素を経済に見合う形で回収できる技術がないため，回収されずに廃棄されてしまっている。

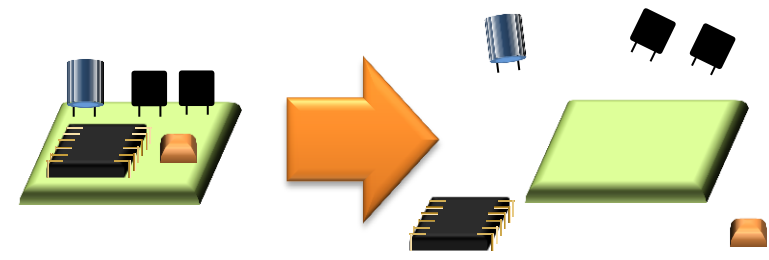
➔ 粉砕，選別等の適切な中間処理技術開発が必要となる³³

基板上の部品剥離・破壊パターン

部品剥離



基板から部品が剥離する



- HC
- CFS
- PS

素材単離



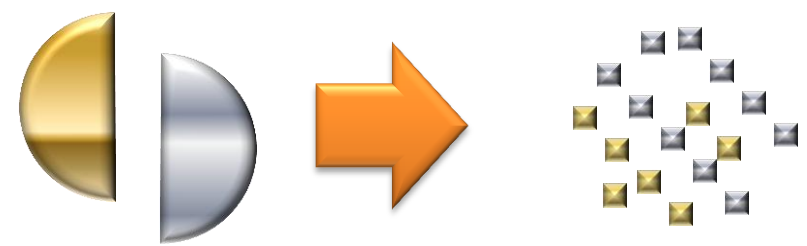
部品が素材ごとに単体分離する



過粉碎



素材がさらに破壊されるor基板上で部品が破壊される



BM